

# **Synthesis and Design of Up-conversion Nanostructures and their Luminescence properties**

**A Dissertation submitted**

**By**

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**Reg. no: 14ETPM02**

**In partial fulfillment of the requirements for the award of degree of**

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**in**

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**of**

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**August 2020**

## Declaration

I hereby declare that the subject manifested in the dissertation entitled “**Synthesis and Design of Upconversion Nanostructure and their luminescence properties**” is the result of the research work carried out by me under the supervision and guidance of Dr. Pradip Paik, Associate Professor, School of Engineering Sciences and Technology, University of Hyderabad, Hyderabad, India for the partial fulfillment of the requirements for the award of Degree of Doctor of Philosophy in Nanoscience and Technology. The work done and the results reported here are original and have not been submitted in part or in full to this university or any other University or Institution for award of any degree or diploma.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of their investigations.



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## **CERTIFICATE**

This is certified that the thesis entitled “**Synthesis and Design of Upconversion Nanostructure and their luminescence properties**” Submitted by **Monami Das Modak** bearing registration number **14ETPM02** in partial fulfilment of the requirements for award of **Doctor of Philosophy** in the **School of Engineering Sciences and Technology** is a bonafide work carried out under my supervision and guidance.

Parts of this thesis have been:

### **A. Published Papers:**

1. UCN–SiO<sub>2</sub>–GO: a core shell and conjugate system for controlling delivery of doxorubicin by 980 nm NIR pulse; Pradip Paik, K. Santhosh Kumar, **Monami Das Modak**, Koushi Kumar and Somedutta Maity; *RSC Adv.*, 2018, 8, 37492.
2. Graphene Oxide for Biomedical Applications; Santhosh Kumar K, **Monami Das Modak** and Pradip Paik; *Mini review: Journal of Nanomedicine research*, 2017, 5, 00136.
3. Self-assembled pearl-necklace patterned upconverting nanocrystals with highly efficient blue and ultraviolet emission: femtosecond laser based upconversion properties; **Monami Das Modak**, Ganesh Damarla, Somedutta Maity, Anil K Chaudhary and Pradip Paik; *RSC Advances.*, 2019, 9, 38246-38256.

### **B. Under Communication:**

1. Multidimensional NaYF<sub>4</sub>:Yb,Er superlattices: Upconversion emission studied through femtosecond-laser treatment; **Monami Das Modak**, Anil Kumar Chaudhary and Pradip Paik.
2. Upconverting nanodots of NaYF<sub>4</sub>:Yb<sup>3+</sup>Er<sup>3+</sup>; Synthesis, characterization and UV-Visible luminescence study through Ti: sapphire 140-femtosecond laser-pulses; **Monami Das Modak**, Anil K Chaudhary, Ganesh Damarla, K. Santhosh Kumar, Somedutta Maity and Pradip Paik; assigned in arxiv with permanent identifier 2008.06783.

### C. Book chapter (Accepted):

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**Monami Das Modak**, Pradip Paik.

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2. 4<sup>th</sup> International Conference on Nanotechnology for Better Living, NBL (2019) 2019; IIT-Kanpur; 6<sup>th</sup> to 7<sup>th</sup> April; *Structural and spectroscopic Properties of up converting nanoparticles: Thin-Film spectra under Femtosecond laser source*; **Monami Das Modak**, Damarala Ganesh, Anil Kumar Chaudhary and Pradip Paik.
3. 3<sup>rd</sup> International Conference on Advanced Materials (ICAM 2019); 2019; 9<sup>th</sup> to 11<sup>th</sup> August; *Optical properties in upconverting nanoparticles*; **Monami Das Modak** and Pradip Paik.
4. International Conference on Functional Materials (ICFM-2020); 2020; IIT Kharagpur; 6<sup>th</sup> to 8<sup>th</sup> Jan; *Formations of highly fluorescent Upconverting nanoparticles (UCNPs)*; **Monami Das Modak** and Pradip Paik.
5. International Conference of Water energy and Environmental sustainability (WEES 2020) 13<sup>th</sup> to 15<sup>th</sup> Jan; *NIR-UV /Visible Emissions from Newly Synthesized Upconversion Nanonecklaces: Irradiations with 140- Femtosecond Pulsed-Laser*; **Monami Das Modak**, Anil K Chaudhary, Pradip Paik.

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2. Stable upconversion nanoparticle dendrimer (UCND) & method of making thereof; Ref. No./Application No.- 201841037609

3. upconversion nanoparticle DOT (UCN – DOT) of size 3.5 nm & its preparation process thereof; Ref. No./Application No.- 201841037608

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| MT-854      | Powder Metallurgy and Ceramics                            | 04      | Pass      |
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| MT-454      | Material Characterization - II                            | 04      | Pass      |
| MT-457      | Powder Metallurgy                                         | 04      | Pass      |



## CERTIFICATE

This is to certify that the work contained in this Dissertation Entitled, "**Synthesis and Design of Upconversion Nanostructures and their Luminescence Properties**", has been carried out by **Ms. Monami Das Modak** (Reg. no.: 14ETPM02), under our supervision and the same has not been submitted for the award of research degree of any university. This dissertation is free from plagiarism and has not been submitted previously in part or in full to this or any other University or Institutions for the award of any degree or diploma.

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DEDICATED  
TO  
MY PARENTS, MY HUSBAND,  
AND MY SISTER

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## Abstract

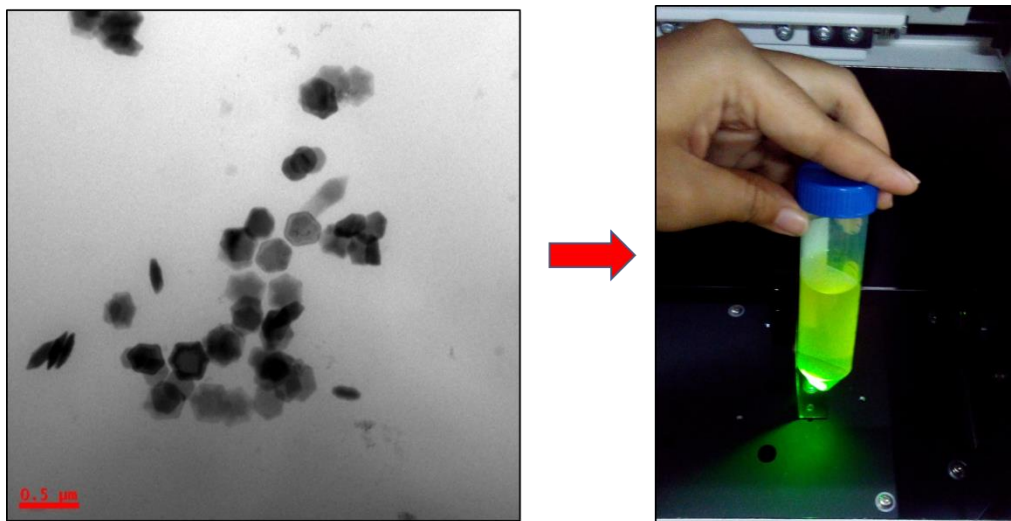
Recently there have been many innovations in research on up converting nanoparticles (UCNPs) doped with Lanthanoids (mostly  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ ) through several synthetic approaches. A set of total 17 chemical elements (15 Lanthanides + Scandium +Yttrium) show up conversion phenomena by exciting with NIR radiation (lower energy, longer wavelength) which finally results in UV or visible light emission (higher energy, shorter wavelength) and makes them highly suitable for various applications. It is well known that for biological studies fluorescence/luminescence -imaging is an important phenomenon. Traditionally, high-energy photons used as excitation which results in low energy emission by down conversion process. But, this phenomenon causes some difficulties like short tissue penetration depth, lower photochemical stability, lower sensitivity, cell death, DNA damage due to excitation with higher energy. In contrast, up-conversion luminescence imaging gives better tissue penetration depth, good photochemical stability, improved sensitivity and very less probability of DNA damage and cell death, as excitation is done with low energy photons and can be used in cancer therapy for destroying cancer cells with the emerging higher energy radiation.

However, these applications are based on the emerging properties of synthesized UCNPs and obviously on their spectral properties along with fluorescence /luminescence imaging. Therefore, synthesizing UCNPs in a precisely controlled manner really remains a challenge.

The current thesis focuses on the preparation of different UCNPs synthesized with novel, one pot chemical synthesis approaches, their characterizations and spectroscopic properties along with their up-conversion fluorescence or up-conversion luminescence.

**Part-I: Synthesis of pure hexagonal -UCNPs with highly efficient upconversion fluorescence/luminescence:**

In this part the novel synthetic procedure for preparation of UCNPs are explained with their characterization and efficient upconversion fluorescence in presence of continuous wavelength (CW) NIR laser source. The formation of a complete hexagonal phase, plate- like UCN nanocrystals, which can exhibit fluorescence even with laser power density of about  $< 50 \text{ mW/cm}^2$ , is introduced.



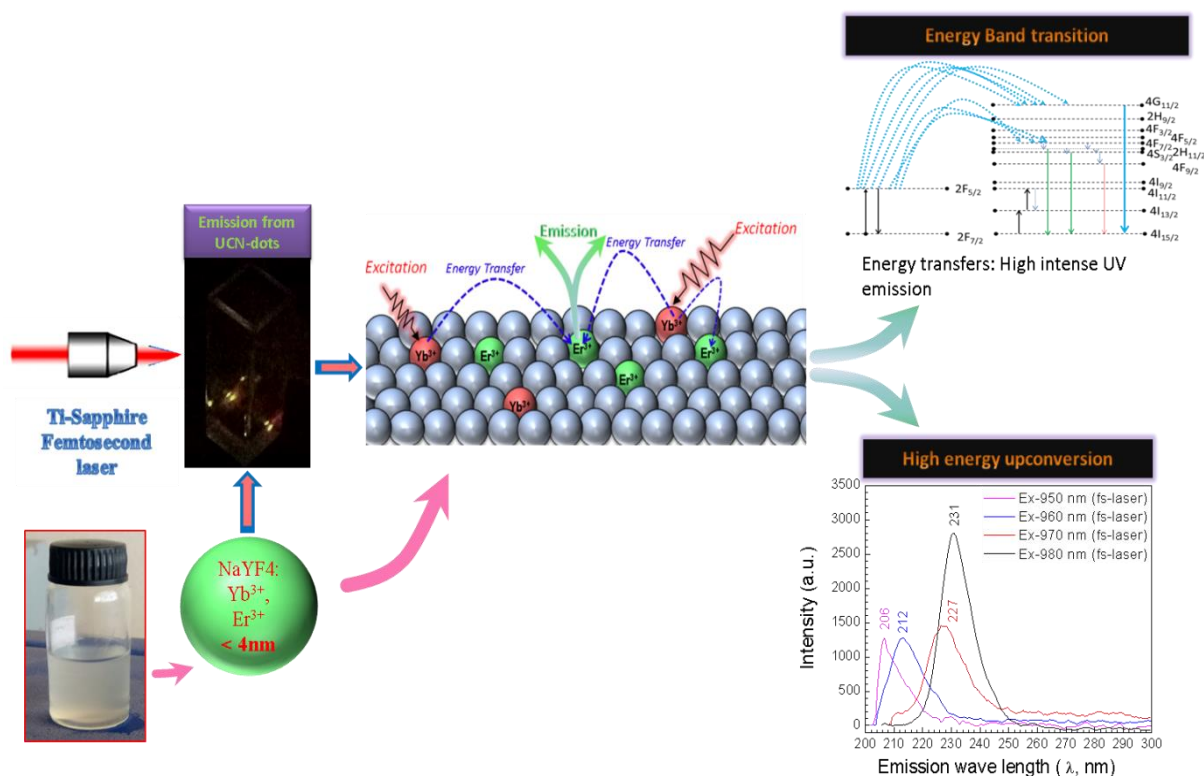
**TOC 1: Figure represents the plate-like formation of UCNPs and their highly efficient fluorescence under 980nm NIR source.**

Uniform hexagonal plate-like structures of  $\text{NaYF}_4$ : Yb, Er UCNPs have been observed with thermal decomposition procedure. These nanocrystals show strong visible upconversion fluorescence even with low power density ( $< 50 \text{ mW/cm}^2$ ) of NIR laser. The high quality UCNPs were prepared by varying the surfactant concentrations based on previous literatures. Hence, the strategy was to consume all the fluoride reagents and then to increase the reaction temperature for improving the quality of synthesized nanocrystals. The maximum temperature

was maintained maximum upto 300 °C. The high crystallinity was confirmed with TEM and XRD analysis. These synthesized nanocrystals have great prospect in bio-imaging probes and fluorescent-labeling.

## Part II: Upconverting nanodots and generation of high energy upconversion through Ti: sapphire 140-femtosecond laser pulses

This part explains synthesis of upconverting nanodots and characterization and upconversion properties.

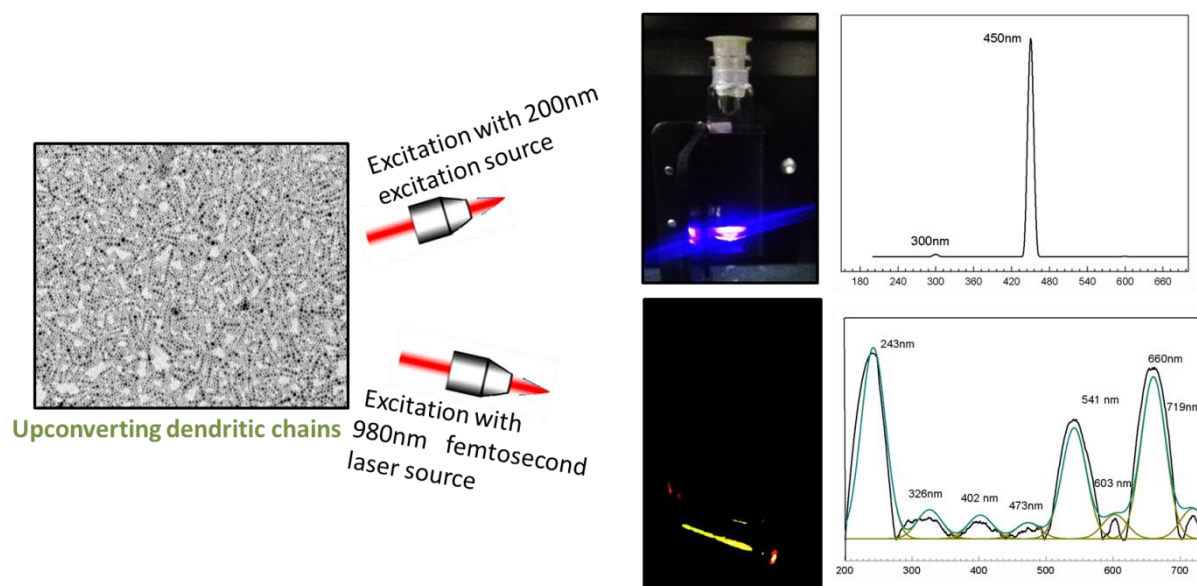


**TOC 2: Figure represents the upconversion mechanism in UCN-dots (below 4nm) by different energy transferring processes**

In this part of the work, dot-sized upconversion nanocrystals (UCN-dots) with diameter c.a.  $3.4 \pm 0.15$  nm of  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  have been synthesized. These UCN-dots exhibit blue-visible emissions under excitation with 830 nm CW-NIR laser source. Further, these UCN-dots exhibit upconversion in UV-region with Ti-sapphire femtosecond laser of 140-femtoseconds duration at 80 MHz repetition rate. This work also reports the shifting of generated UV emissions by tuning the excitations 950, 960, 970, and 980 nm irradiated from Ti: sapphire femtosecond laser under incident pump powers 1.09, 1.00, 0.955, 0.900 W, respectively and resulted an increased internal-UCQY and external-UCQY with increasing the irradiances. Further, the photo luminescence of UCN-dots in visible region has also been studied. The generation of up-conversion in UV and blue emissive regions and high UCQY could be useful further for designing optoelectronic and biomedical devices for therapeutic and for other various applications.

### **Part III: Self-organized dendritic-upconverting nanocrystals with highly efficient blue and Ultraviolet emission**

This work reports a new finding on the formation of self-organized upconversion nanodendrites (UCN-Ds) which exhibit strong visible emission under 980 nm NIR excitation source. Each nano-dendrite consists of several upconversion nanoparticles(UCNPs) having size c.a.  $11 \pm 2$  nm. UCN-Ds are arranged in a self-organized manner to form necklace type chains with an average length of 150nm. Further, UCN-Ds are comprised of almost 7 UCNPs with an average particle separation  $\sim 4$  nm in each of the dendritic chain. Spectroscopic properties have been studied. Interestingly, these UCN-Ds exhibit high energy upconversion especially in UV region on interaction with  $\sim 140$  femtosecond pulse duration at 80 MHz repetition rate and intense blue emission at 450 nm on interaction with 200nm excitation source . The preparation of self-assembled dendritic UCNPs is easy and they are very stable for a long period of time.



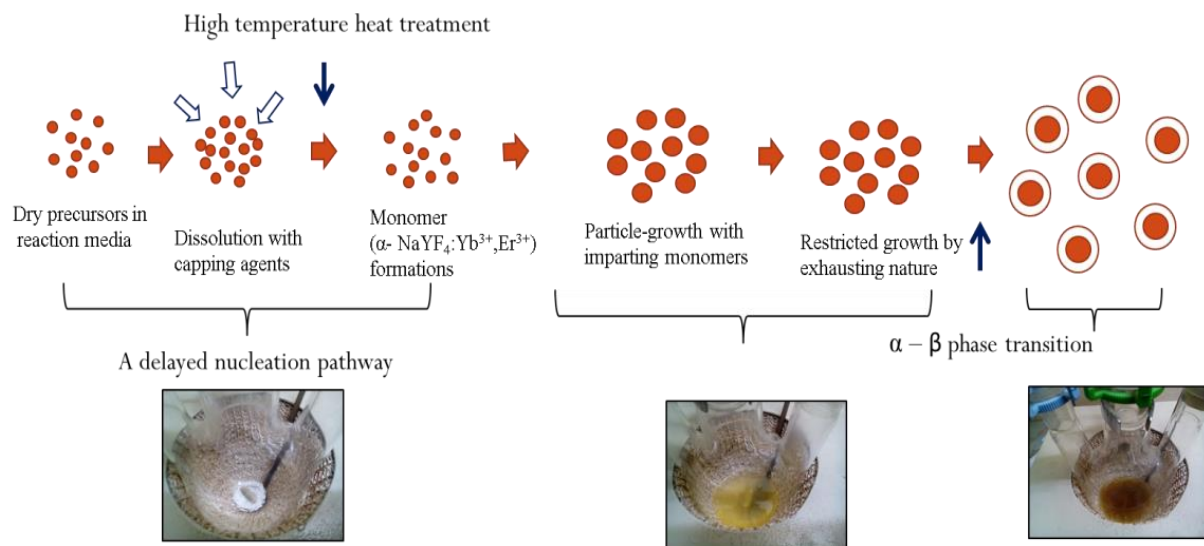
**TOC 3: Figure represents the dendritic formations of UCNPs (UCN-Dendrimers) and their efficient blue emissions**

Emission (fluorescence/luminescence) intensity is high which can make them a suitable unique agent in innumerable number of industrial and bio-applications .

#### **Part IV: Morphologically controlled upconverting self-assembled superlattices (SAM-SL UCNPs) prepared by one-pot chemical approach: Efficient luminescence observed under different pump powers**

Herein this work reports on the self-assembled and in-situ formation of superlattices of upconverting nanophosphors over multiple-magnified scales prepared by one-pot chemical approach. The synthesis method is optimized. The as-synthesized nanophosphors can display sharp and bright luminescence (both in ultraviolet and visible region) and fluorescence (mostly in visible region) under Ti-Sapphire 140-femtosecond laser pulses at 80 MHz

repetition rate with 950nm-990nm excitation wavelengths and under 980nm continuous wave laser sources, respectively.



**TOC 4: Figure represents schematic of the whole process succeeding the nucleation and growth mechanism along with  $\alpha$  -  $\beta$  phase transition in morphologically controlled self assembled superlattices (SAM-SL-UCNPs).**

The mean particle-sizes are varied from 5-8nm. Further, the growth mechanism of differently synthesized superlattices of NaYF<sub>4</sub>:Yb,Er has also been elucidated. The internal and external quantum yield of the self-assembled superlattice structure have been expounded with different laser irradiation. The substantially improved design of nanophosphors will boost biological and energy related nanophosphor applications.

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# **1 INTRODUCTION AND LITERATURE REVIEW**

## **Outcome:**

**Monami Das Modak**, Pradip Paik, Review article: A wide portray of upconversion-nanoparticles with their several synthetic procedures and biological applications, Manuscript accepted.

**Monami Das Modak**, Pradip Paik, Upconversion nanoparticles: synthetic procedures and properties for biological applications, conference proceedings, THEME: Advanced Nanomaterials ICONSEA-2018, ISBN No.978-81-924726-4-5

Present-days have spotted many innovations in research on upconverting nanoparticles (UCNPs) co-doped with Lanthanoids (mostly  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  /  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ ) through several synthetic approaches. A set of total 17 chemical elements (15 Lanthanides + Scandium + Yttrium) show upconversion phenomena by exciting with NIR radiation (lower energy, longer wavelength) and finally results in visible light (higher energy, shorter wavelength) which makes it highly delightful for various applications. It is well known that for biological studies fluorescence-imaging is an important phenomenon. Traditionally, as excitation radiation high energy lights are used which result in low energy emission by downconversion process. But, this phenomenon causes some difficulties like short tissue penetration depth, lower photochemical stability, lower sensitivity, cell death, DNA damage due to excitation with higher energy, whereas upconversion luminescence imaging gives better tissue penetration depth, good photochemical stability, improved sensitivity and very less probability of DNA damage and cell death as herein excitation is done with low energy photons and can be used in cancer therapy for destroying cancer cells with the emerging higher energy radiation. Herein this review several current progresses with Upconversion nanoparticles (UCNPs) in recent applications along with their different synthesis procedures, optical properties and growth of erection methods of different UCNPs applications have been highlighted based on their immobilization strategy.

Upconverting nanoparticles (UCNPs) have already been established for prospective use as bio-labels and in biological analysis and bio imaging which are the most promising technologies today. These promising and advanced technologies suggest that UCNPs could reconstruct the enduring technologies due to their ability to suspend as clear colloidal solutions [1]. Until now, the highest upconversion efficiencies have been reported in  $\text{NaYF}_4$  hexagonal phase co-doped with  $\text{Er}^{3+}/\text{Yb}^{3+}$  or  $\text{Tm}^{3+}/\text{Yb}^{3+}$  ion-pairs [2][3].

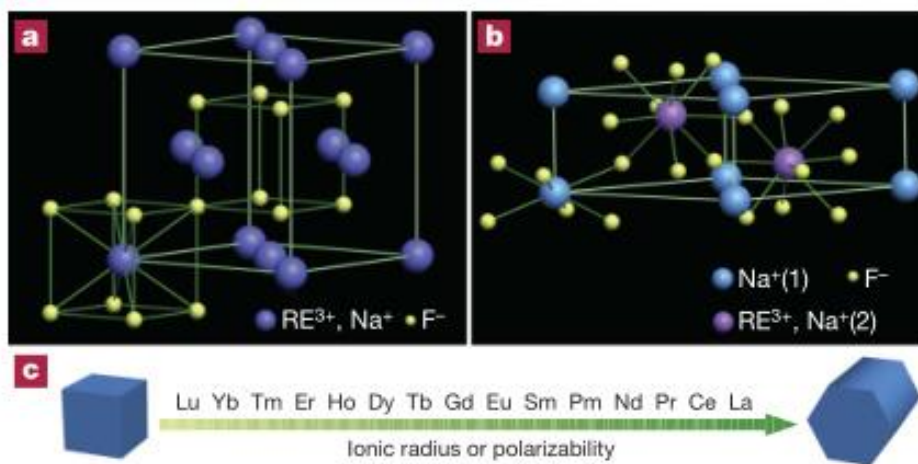
Selection of host material is an important factor for achieving Upconversion phenomenon properly. To achieve highest luminescence quantum yield and less probability of occurrence of non- radiative relaxation, nowadays fluoride is used in host materials such as

REF<sub>3</sub> and AREF<sub>4</sub> (A=Alkali). As a result, they help to increase refractive index and transparency. Though Chlorides and Bromides can also enhance luminescence intensity, but they are mostly sensitive to moisture, so difficult for imaging bio-molecules. Therefore, adding of fluoride in host materials is an increasing phenomenon today. Photon Upconversion process is based on non-linear optics, where the optical properties of material changes with the intensity of the incident exciting light. But are they noteworthy and adaptable enough to explain the difficulties of redirecting to a new technology, conventionally a lengthy and precious procedure? Could UCNPs become the upcoming wild materials reconstructing some of the contemporaneously used technologies and leading to the advanced research? Is it flexible as many as required to transmute many features in our life? By reviewing different proposed synthetic procedures, allowing their several applications in different fields those questions will be answered. Though there are several synthetic routes for preparing UCNP nanocrystals, among which hydrothermal synthesis has a lot of favorable advantages compared to the low reaction temp process (< 250°C); and it resulted in uniform distribution of size, shape and morphology. The procedure and the experimental set-up used in these methods are easy to handle and very simple. In such case, basically three conditions are responsible to convert alpha ( $\alpha$ - NaYF<sub>4</sub>) phase to beta ( $\beta$ - NaYF<sub>4</sub>) phase, they are high hydrothermal temperature, long hydrothermal time and high fluoride to lanthanide molar ratio [4].

So initially, the observed properties in UCNPs will be discussed.

By Raman spectroscopy, it has been confirmed that the dominant phonon modes in undoped NaYF<sub>4</sub> lie in the range 300- 400 cm<sup>-1</sup>. These low energy phonon modes describe the remarkable Upconversion efficiency [5]. By the implementation of the plasmonic effects, it is possible to enhance upconversion fluorescence which has been already done by directed nano-assembly of NaYF<sub>4</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> nanocrystals with gold nanospheres [6]. From literature it has been observed that, crystallographic size, crystallographic phase (Schietinger et al., 2010) and optical emission properties of such resultant nanocrytals can be controlled simultaneously by influencing them with dopant ions[7]–[11]. By controlling concentration of trivalent

lanthanide dopant ions, it is quite possible to tune size (down to 10 nm), shape (cubic to hexagonal) and upconversion emission colour (green - blue) of NaYF<sub>4</sub> nanocrystals [12]–[14]. There are two factors of dopant ions their size and dipole polarizability that can change the crystal size and shape of resultant nanocrystals. UCNPs can offer high photochemical stability, sharp emission bandwidths and large anti-stokes shift [15]. There are four experimental variables which are, solvent in nature, reaction time and temperature, metal precursor concentration that inflict stiff sway over crystallization of resultant particles with completely explained crystal phase and size. Hexagonal UCNPs phase structure is always preferable compared to cubic structure in various applications. There is a huge difference (almost by a factor 7.5) in fluorescence intensity between its cubic and hexagonal phase - nanoparticles [16]. Despite these drawbacks, in cubic-phase, sometimes we prefer cubic phases in as-synthesized UCNPs depending on their particular sizes, shapes, crystallinity, fluorescence properties and easy dispersion in non-polar solvent. Generally, it has been noticed that the structure of NaREF<sub>4</sub> system for both cubic and hexagonal phase differ on the basis of F<sup>-</sup> cubes and ions present in them. In cubic structure, cations and vacancies sustain with uniform numbers of F<sup>-</sup> cubes whereas for hexagonal structure, F<sup>-</sup> ions are seated in an ordered array, to fit the structural change, electron cloud deformation of cations is crucial (figure 1.1.1). Basically, one ordered way is maintained for lanthanides. As Lanthanide series start from Lanthanum (La), finishes with Lutetium (Lu) (Lanthanide series-La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), now if we move towards higher atomic no. and lower atomic mass i.e. from La to Lu, weight will decrease and ionic radii will increase, dipole polarizability increases, tendency towards e<sup>-</sup> distortion cloud increases which is the appreciative condition for hexagonal phase. So, formation of hexagonal phases in Lanthanides having higher atomic number will be more than that of having lower atomic number. Size of Y<sup>3+</sup> ion is ( $r = 1.159 \text{ \AA}$ ) in NaYF<sub>4</sub> host lattice. More hexagonal phases will be produced for doped lanthanide ions having larger size (i.e. for Gd<sup>3+</sup> ion  $r = 1.193 \text{ \AA}$ ) than the size in Y<sup>3+</sup> in host lattice and finally the growth of unit cell volume occurs due to the presence of larger sized lanthanide dopant ions [15].



**Figure 1.1.1: Schematic of phase transformation in Na [Rare Earth (RE)] F<sub>4</sub> while doped with lanthanides, (a) Cubic phase, cations and vacancies sustain with equal numbers of F<sup>-</sup> cubes, (b) Hexagonal phase, two types of cation sites sustain with an ordered F<sup>-</sup> ion- array (Na<sup>+</sup>, RE<sup>3+</sup>/ Na<sup>+</sup>), (c) Shows the fashion of cubic - to - hexagonal phase transition as a function of ionic radius / polarizability of elements present in lanthanoid-series. Reproduced with permission (Wang et al., 2010). Copyright: Nature publication**

## 1.1 Challenges in production

There are several applications of UCNPs having different shapes, sizes and structures, which can be significantly controlled by their development with a number of designed synthesis procedures and their dispersions in various media. Now depending on the notable properties and the quality of UCNP (either in dried or in colloidal form) in as-synthesized materials they can be used in different potential applications such as in silicon based solar cell as spectral converters[17]–[31], in optical imaging and MRI as a multimodal contrast agent [32], [33], in FRET Biosensors[34]–[39]; as Colour display[10], [40]–[45], versatile bio-probes in Biomimetic surface – engineering[46], nanoprobe for sensing and imaging of pH[47]–[51], cells and small animals[52]–[54], nano-transducers for killing diseased cells in deep tissues [55], the most viable luminescent bio-labels in bio-conjugation and bio-imaging [56]–[63].

Therefore, the production of those UCNPs with required sizes, shapes and structures is very crucial for different applications. During their preparation, all the reaction parameters are being controlled in a precise manner due to the high sensitivity of the products through their formation periods. Thus, the production of UCNPs is challenging.

If we go through the literature reviews, we will find that mostly several optical properties became prominent for their applications. This is the main property for which they are being broadly used in nanotransducers[55], [64]–[67], broad bands[23], [25], [68], [69], Imaging contrast agent [33], multimodal imaging [70],[71], superresolution- nanoscopy [72][73], imaging probes [74], and so on. Therefore, review has been focused briefly on optical properties with possible photonic processes for UCNPs.

## 1.2 Optical properties

Lanthanoids exist in Lanthanide series and there are total of 15 lanthanoids. Though transition metals (Scandium, Yttrium) , where atoms have partially filling ‘d’ sub-shell and elements in actinide series can exhibit Upconversion phenomena, but specially RE elements having combination of 15 lanthanoids + Scandium + Yttrium, a set of total 17 chemical elements show Upconversion phenomena very strongly, i.e. by exciting that Lanthanide doped nanocrystals with NIR radiation. In the Upconversion process, we can get visible light with the emission of higher energy photons. Thus, Upconversion process converts low energy, long wavelength NIR radiation to high energy, short wavelength visible light. The optical properties of Upconversion nanoparticles arise due to conversion of Near Infrared radiation (NIR) into visible spectral range, which is a very efficient phenomenon in rare-earth based materials. The nanocrystals based on rare-earth ions showed strong Upconversion emission with a continuous excitation wavelength at 973 nm [6]. Therefore, they have a great potential in applications of solid-state laser materials as well as several lighting, panel and colour display technologies [75]–[77]. It is well known to us that NaYF<sub>4</sub> nanocrystals co-doped with Yb<sup>3+</sup> and Er<sup>3+</sup>/Tm<sup>3+</sup> are the most promising Upconverting nanomaterial today as these

nanocrystals are sensitized by  $\text{Yb}^{3+}$  (sensitizer) and multicolor wavelength range can be distinguished from  $\text{Er}^{3+}$  or  $\text{Tm}^{3+}$  (activator) dopant ions.

Experimentally and theoretically it has been already proven that most of the lanthanide ions exhibit visible light under excitation with NIR radiation but sharp luminescence imaging can be observed by Upconversion process under 980nm excitation if some of them such as  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  are co-doped with the host lattice like  $\text{NaYF}_4$ , hence the productive forms are written as  $\text{NaYF}_4: \text{Yb}^{3+}; \text{Er}^{3+}$  /  $\text{NaYF}_4: \text{Yb}^{3+}; \text{Tm}^{3+}$ .

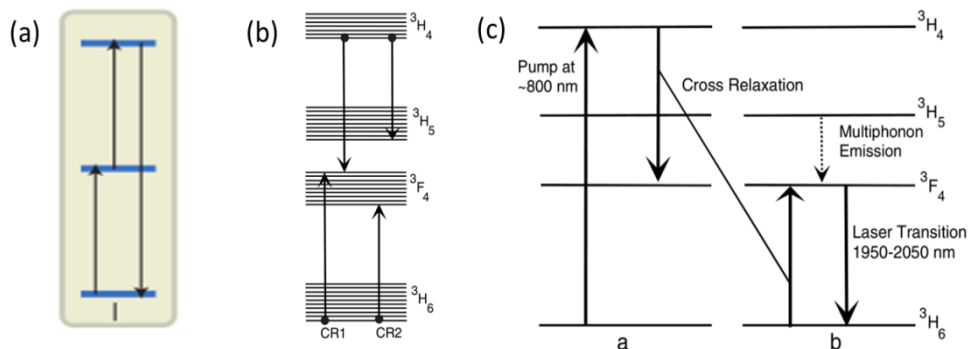
Some important luminescence properties can be observed with using such UCNPs such as narrow band width with shorter wavelength compared to the excitation wavelength i.e. anti-stokes type emission and long-time emission [12][78]. To get Upconversion phenomenon properly, choosing of host material is an important factor. To achieve highest luminescence's quantum yield and also less probability of occurring non-radiative relaxation nowadays fluoride is used in host materials such as  $\text{REF}_3$  and  $\text{AREF}_4$  ( $A=\text{Alkali}$ ), as a result they help to increase refractive index and transparency though chlorides/ bromides can also enhance luminescence intensity. However, they are very sensitive to moisture and possess difficulty for imaging of bio-molecules and cells. To overcome this limitation, fluoride molecules are added in the system. The main difference between fluorescent and luminescent materials is their different characteristics. Fluorescent materials absorb high-energy photons with the emission of visible light and low energy photons, which results in auto fluorescence, wide emission bands and limited sensitivity. To overcome these difficulties Upconverting luminescent nanoparticles with high quality developed promptly. Trivalent rare earth (RE) ion ( $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ) follows Upconversion process fairly [79]. By incorporating a few energy-transfer related mechanisms, we will try to understand the photon-generation mechanism in UCNPs.

There are some basic mechanisms which results in highest population in excited state and after that when they come in the ground state, emit high-energy photons. Multiphoton absorption occurs by the Excited State Absorption Mechanism (ESA) [79] (figure 1.2.1) which further involves multistep excitation by the same ion and finally highest population

occurs at the excited state. This process is also known as phonon assisted electronic transitions [75][79].

Suppose, Energy of incident photons has flux  $\phi$  (Say) is resonant with the energy difference ( $E_1 - E_0$ ), then some of the photons are absorbed from the ground state by the particular ion. Similarly, while the energy of the incident photons having certain flux resonant with the energy difference ( $E_2 - E_1$ ), then only incoming photons can be absorbed in the intermediate state by the same ion. Now the population in the excited state becomes high and consequently the ion reaches to its high-excited state, but this phase is not stable from this excited state and finally, upconversion luminescence occurs by radiating photons. We have considered this process for a single ion so we can assume that it is independent on ion-concentration. According to literature, anti-stokes fluorescence is proportional to the incident photon flux such that, for above-mentioned case fluorescence is directly proportional to the square of the incident photon flux. ESA process is quite relative with the laser pumping process. As it avoids transfer losses, so it is assumed to be a suitable pumping process for Upconversion single-doped mechanism. In ESA case, finally we can conclude that by absorbing atleast two photons having sufficient energy, a single ion can reach its emitting level from which it undergoes luminescence.

In photon avalanche process (PA) four energy states are involved instead of three as in ESA. Cross relaxations (CR) and Energy transfer process are very important in upconversion phenomenon. Cross Relaxation occurs due to overlapping of the spectra. For example, in Silica between  $3H_4 > 3F_4$  Fluorescence spectra there is a strong overlapping between them. Previously it has already been examined for  $Tm^{3+}$  doped silica fiber lasers[80]. The cross-relaxation mechanism with its energy level diagram of the four multiplets  $3H_6, 3F_4, 3H_5, 3H_4$  is shown in figure 1.2.1.



**Figure 1.2.1: (a) Excited State Absorption Mechanism (ESA). Reproduced with permission. Copyright: Nature Materials publication, (b) Detailed energy level diagram of the four multiplets of the  $Tm^{3+}$  ion. Reproduced with permission. Copyright: Optics Communications publication, (c) Two Energy Transfer Upconversion Processes (ETUs). Reproduced with permission. Copyright: Optics Communications publication**

Unlike ESA, (figure 1.2.1) where Energy Transfer Upconversion process ETU is a pump power independent process and it involves two ions system – one is sensitizer ion and another one is activator ion. Sensitizer ion (S) can transfer its energy to activator ion (A) as they are placed much closer to each other. On excitation with suitable light “A” goes from its ground state to excited state and it is only possible if excited energies of two ions are equal or nearly equal to each other. After reaching the excited state, S ion can transfer its energy to the nearly placed A-ion whose excited state energy are equal. Here it is to be notified that before emitting photons by S-ion, A goes from ground state to the excited state.

Several spectral properties of RE doped UCNPs have huge scope in biomedical imaging and therapeutics [80]–[83]. Other exciting optical properties in the same material can be aroused by tuning their spectral properties in a proper way. Surface Plasmon resonance caused by the interaction of metal with the incident light assist for different interesting optical events like radiative and non-radiative properties of nanocrystals[84]–[86]. In literature, the Raman spectroscopy with dominant phonon modes ( $300cm^{-1}$  -  $400cm^{-1}$ ) of such RE based materials has been already demonstrated [5].

### 1.3 Different synthetic strategies for the production of Upconversion nanoparticles

Earlier we have already discussed, choosing of host materials is a very important factor to UCNPs as they determine their quality. Now to get better quality (such as better luminescence efficiency, chemical stability, low phonon energies giving low probability of non-radiative decay) synthesizing UCNPs in a proper way is very crucial key. Synthetic routes for Upconversion nanoparticles are based on mainly three strategies, thermal decomposition, Hydrothermal or solvo-thermal synthesis, ionic –liquid based or ionothermal synthesis. Hence, we will discuss a variety of synthetic routes based on those three basic strategies.

#### 1.3.1 Thermal Decomposition

To control the shapes and sizes of nanocrystals, thermal decomposition is one of the most familiar and popular method. As reagents, organic precursors (e.g. trifluoroacetate precursor), surfactants (oleic acid, oleylamine) and organic solvents are used. By product, what we get is nuclei form of our desired nanocrystals, which then goes under growth mechanism. There after dissolution and aggregation take place. Thermal decomposition follows overall four stages- Nucleation, Growth, Dissolution and Aggregation

Most of the RE fluorides are synthesized by this route. Some examples of such prepared UCNPs are NaYF<sub>4</sub>:Yb,Er; NaYF<sub>4</sub>:Yb,Tm; NaGdF<sub>4</sub>:Yb,Er; NaGdF<sub>4</sub>:Yb,Tm ; NaLuF<sub>4</sub>:Yb,Er; NaLuF<sub>4</sub>:Yb,Tm,CaF<sub>2</sub> etc .

**Drawbacks of thermal decomposition:** Though thermal decomposition[1][87] gives well shaped and sized monodispersed particles (Barnes et al., 2003) but still it holds some disadvantages like-

- a) Requires temperature in the range of 250°C - 330°C, which is quite high. During maintenance such high temperature sometimes may cause burning, particle-aggregation, particle enlarging.
- b) Surfactants having long hydrocarbon chains and polar capping groups associated with organic precursors during synthesis can yield difficulties for biological applications especially while we are using them for stabilizing nanomaterials.
- c) Requires high-boiling organic solvents to dissolve organic precursors.
- d) To overcome the difficulty of using surfactants sometimes we need surface modification/ engineered modified surface that can be cost-effective.
- e) Ideal condition of this experimental set up is always being used in an complete oxygen-free inert gas condition which is difficult to handle during synthesis, even a very small amount of oxygen during synthesis may damage and form an unsuccessful product.

In spite of having the above mentioned drawbacks in thermal decomposition procedure, this process has already been investigated with the production of Alpha-NaYF<sub>4</sub>:20%Yb,2%Er (cubic-phase) and Beta-NaYF<sub>4</sub>:20%Yb,2%Er (hexagonal-phase) nanocrystals in a large-scale area where successful synthesis of co-doped NaYF<sub>4</sub> nanocrystals has been built-up with thermal decomposition procedures. The final shapes, sizes and structures of UCNPs can be changed by modifying or varying the reaction time, reaction temperature, reagent concentration and the resulted modified nanocrystals can be characterized using Transmission electron microscopy(TEM), High-resolution transmission electron microscopy (HRTEM), Field emission scanning –electron microscopy (FESEM) and X-ray diffraction (XRD) patterns.

By introducing two synthetic procedures, collecting from different literature[1], [88], [89], hereby I will describe the thermal decomposition with their required precursors, reaction

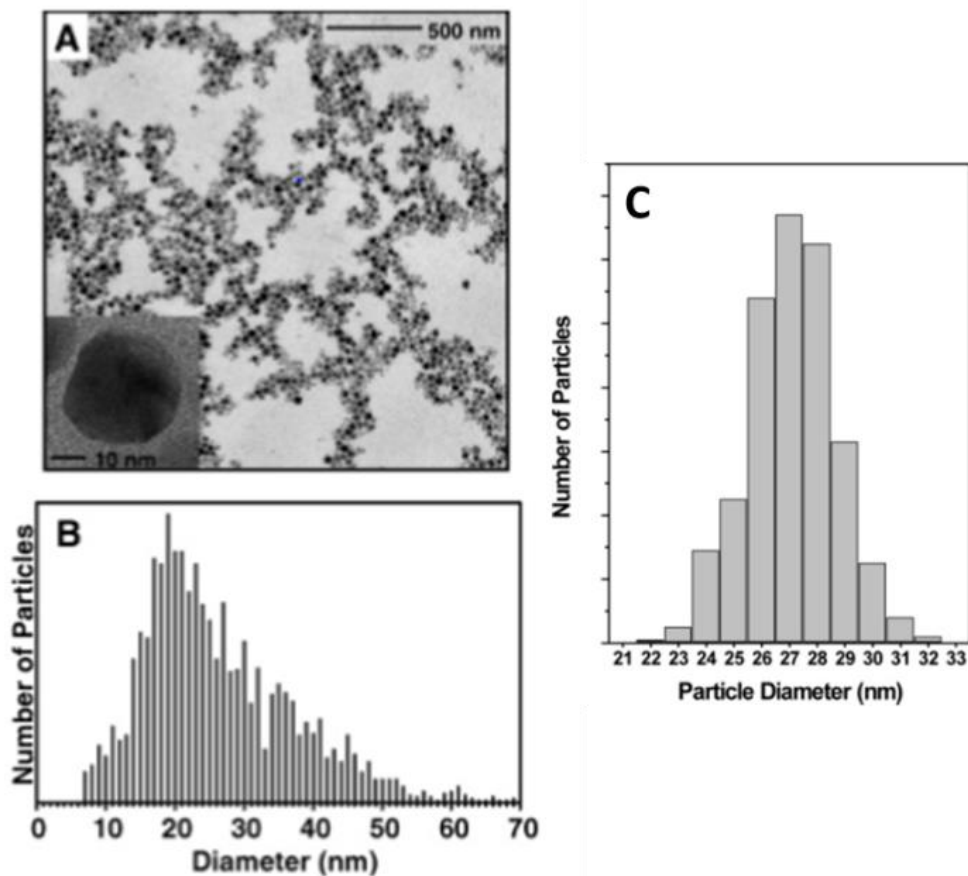
temperature and reaction time. At a recent time, Gudel et al. [1], [2], [4], [90] spotted micrometer sized hexagonal phases of  $\text{NaYF}_4: \text{Yb}^{3+}, \text{Er}^{3+} / \text{Tm}^{3+}$  crystals which are enable to show highest Upconversion efficiencies. It is familiar to us that metal trifluoroacetates thermally decompose providing their corresponding metal fluorides, fluorinated and oxyfluorinated carbon species, whereas lanthanide trifluoroacetate precursors can be formulated from their corresponding lanthanide oxides and trifluoroacetic acid.

TEM images of the colloidal UCNPs ( $\text{NaYF}_4$  co-doped with  $\text{Er}^{3+}/\text{Yb}^{3+}$  and  $\text{Tm}^{3+}/\text{Yb}^{3+}$ ) formed via thermal decomposition procedure are shown in the figure 1.3.1 with two histograms of particle size distribution (histogram result between Number of Particles and Particle Diameter (nm) for Upconverting Nanocrystals).

### 1.3.2 Hydrothermal or Solvothermal synthesis

A convenient synthesis process for producing UCNPs with overcoming some of the difficulties associated with thermal decomposition process is termed as hydrothermal or solvothermal synthesis procedure. The advantages of this process over thermal decomposition are given by following

- a) Temperature required is relatively low ( $160^\circ\text{C}$  to  $220^\circ\text{C}$ ) compared to that in thermal decomposition.
- b) Oxygen free-inert gas condition is not required and that is why it is easy to handle.
- c) Organic compounds are not required as this process involves water solution phenomena.



**Figure 1.3.1: (A) TEM image, (B) Histogram for obtained particle- sizes with ~1400 nanocrystals. Reproduced with permission (Boyer et al., 2006). Copy right: Journal of American Chemical Society publication (C) Histogram of obtained particle sizes with ~ 500 nanocrystals. Reprinted with permission (Boyer et al., 2007). Copyright : Nano Letters publication**

d) Various nanocrystals with hexagonal and octodecahedral shapes can be formed or synthesized applying this method. By adding several fluoride sources, organic additives (e.g. trisodium citrate) we can get desired shapes and sizes with different morphologies and architectures.

e) Synthesis through hydrothermal/solvothermal synthesis has been given in various literatures [91]–[94].

***Advantages of Hydrothermal synthesis over others and morphological effect of resultant particles on hydrothermal time, temperatures and on other parameters:*** Compared with the other synthetic routes, hydrothermal synthetic procedure is superior following some advantages like,

- a) At relatively lower temperature, ( $< 250^{\circ}\text{C}$ ) synthesis can easily happen and during synthesis by changing concentration of precursors, nature of solvent reaction time and other experimental parameters size, structure and morphology of the resulting products can easily be modified.
- b) Experimentally it has been observed that the purity of the resulting particles become significant in case of hydrothermal synthesis.
- c) The synthetic process and the required equipment used in such experiment are simpler and easier to handle.
- d) Sometimes organic additives (EDTA, citrate) are used during synthesis to get small and uniform particles. The resultant size of particles differs with different organic additives due to their different chelating agent and molecular structure providing morphological product. The main reason behind that difference is the influence of chelator on the growth of particles [95]. As for example, size of the particles synthesized with citrate is much less than that synthesized with EDTA.

There are generally four factors, which substantially affect the size, structure and morphology of the resulting nanocrystals. They are described as follows,

- a) *Effect of fluoride-lanthanide molar ratio:* The amount of NaF content is counted in NaF: Ln molar ratio to investigate its effect on size, structure and morphology of the

resulting UCNPs. Larger the fluoride-lanthanide ratio provides the better crystallization, more regular and smoother surface, more hexagonal phases (i.e. influence the crystal structure as fcc or hexagonal) of the resulting nanocrystals. Now, the effect of NaF: Ln ratio on crystallization, shape and surface pattern of the synthesized  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  co-doped  $\text{NaYF}_4$  nanocrystals is shown in table 1.3.1.

**Table 1.3.1: Different crystallization, shape and surface pattern with different amount of NaF:Ln ratio**

| NaF : Ln<br>molar ratio | Crystallization                                                       | Shape                                 | Surface<br>pattern     |
|-------------------------|-----------------------------------------------------------------------|---------------------------------------|------------------------|
| 4                       | Low crystallization of the sample providing more likely fcc [3], [96] | spherical                             | Coarse surface         |
| 8                       | Improved crystallization.                                             | More regular shape.                   | More smoother surface. |
| 12                      | Further improved                                                      | Pure hexagonal shaped sub-microplates | Further improved       |

From table 1.3.1, it is clear that the effect of NaF content on the crystal morphology plays an important role as the crystal phase is completely transformed into hexagonal phases at the NaF: Ln molar ratio of 12 or above.

b) *Effect of citrate-lanthanide ratio*: In hydrothermal method chelating agent has appreciable effect on size and aggregation of the particles. Therefore, by choosing proper chelating agent it is quite possible to produce small-sized and dispersible nanoparticles[4], [97]. Therefore, citrate: Ln ratio plays an important role in forming different morphologies (table 1.3.2).

**Table 1.3.2: Molar ratio of chelator: lanthanide affecting the morphologies of NaYF<sub>4</sub>: Yb<sup>3+</sup>,Er<sup>3+</sup> nanocrystals**

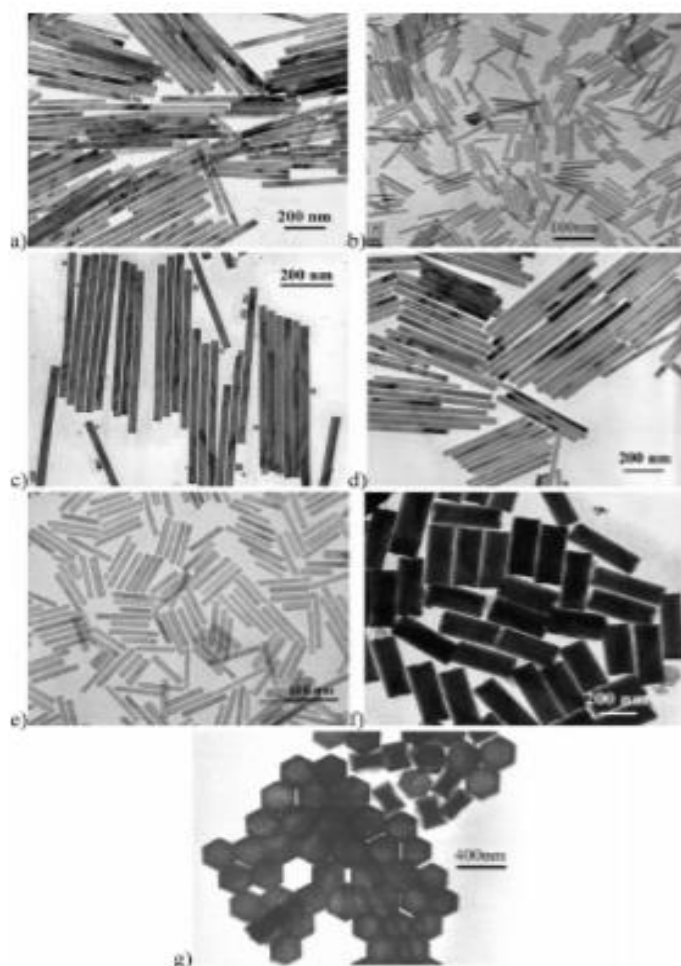
| <b>Molar ratio of citrate– lanthanide</b> | <b>Morphology of the resulting particles</b>                                                                                           |
|-------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| 0:1 (i.e. without citrate)                | Formulation of resulting nanoparticles as mixtures of nanorods as well as spherical nanoparticles.                                     |
| 0.5                                       | A mixture of cubic nanoparticles and hexagonal submicroplates.                                                                         |
| 1.0 and 1.5                               | Development of pure nanoparticles having size distribution in the range between 30-50 nm (With the restriction of the crystal growth). |

In conclusion the formation of cubic crystal structure is possible with citrate lanthanide and ratio is greater than unity (citrate: lanthanide > 1) and with citrate- lanthanide ratio is less than unity there exist mixed phases (cubic and hexagonal) in resulting crystal structure (citrate: lanthanide <1).

c) *Effect of Hydrothermal temperature:* Generally, the hydrothermal required temperature in the range between 160 to 200° C to eventuate phase transformation. At higher hydrothermal temperature cubic to hexagonal phase transformation is possible owing to generation of energy. Lower hydrothermal temperature approves smaller sized nanoparticles having cubic phases, whereas higher hydrothermal temperature approves the formation of nanocrystals and sub-microplate mixture having hexagonal phase.

d) *Effect of Hydrothermal time:* Hydrothermal time affects the crystallization and growth of the resulting nanocrystals. Long hydrothermal duration is favorable for the transformation of cubic phases into hexagonal phases. The hydrothermal time increases

the rate of several processes during synthesis such as dissolution, re-nucleation and crystallization processes. In literature it has been described that pure hexagonal phase – microplates (our required phase) of  $\text{NaYF}_4$  nanocrystals have been found with hydrothermal time around 2 or 2.5 hours (keeping citrate: lanthanide ratio= 1:1; and temperature at  $180^\circ\text{C}$ ) [4]



**Figure 1.3.2: TEM images of the resulted nanocrystals after solvo-thermal treatment. Reproduced with permission (Wang and Li, 2007). Copyright: Chemistry of Materials publication**

TEM images of the Upconversion nanoparticles ( $\text{YVO}_4:\text{Er}^{3+}$ ) synthesized with hydrothermal/solvo-thermal treatment are shown in figure 1.3.2.

### 1.3.3 Ionic-Liquid based or ionothermal synthesis

Although pure hexagonal phase (which can yield better Upconversion than the cubic one) can be obtained by this method, however, it is comparatively less popular than the previous two methods because it holds certain limitations while synthesizing nanocrystals e.g.

- a) Nanocrystals used must be non-flammable
- b) Does not require any organic solvent.
- c) Produced particles become broader in size with lower quality (less uniformity, less monodispersity, less chemical stability) than the other two processes.
- d) Various shapes and sizes cannot be found by using ionothermal synthesis, only water-soluble hexagonal phase formation is possible.

Due to these above-mentioned limitations, it can be used only for preparing a few selective nanocrystals. In spite of having such limitations, few advantages are also present such as

- a) Reaction occurs within a very short period of time.
- b) Requires low temperature range and vapor pressure that are easy to control.

Earlier, synthesis procedures for the production of  $\beta$ -phase  $\text{NaYF}_4$  nanomaterials were developed [16], [91], [96], [98]–[101] with the formation of particles of size  $\sim 15$  nm where most of the synthesis procedures required in high boiling solvents or in their mixtures (e.g., oleic acid, oleylamine, 1-octadecene or their solvent mixtures) owing to co-thermolysis of rare-earth trifluoroacetates and sodium trifluoroacetate [88]. But these resulting luminescent

nanomaterials seems to be difficult while using in bio-probes due to their sizes, not only that but also from literatures it is revealed that they require a very high reaction temperature and yield rather very low compared to the other methods. Therefore, production of smaller size of such nanoparticles with high yield is a demanding matter in Bio-probe imaging. Chow et al. group synthesized 10 nm sized hexagonal phase UCN nanocrystals in oleylamine at temperature above 300°C having very narrow size distribution and introduced multiple precursors e.g., –  $\text{CF}_3\text{COONa}$ ,  $(\text{CF}_3\text{COO})_3\text{Y}$ ,  $(\text{CF}_3\text{COO})_3\text{Yb}$ ,  $(\text{CF}_3\text{COO})\text{Er}$  /  $(\text{CF}_3\text{COO})_3\text{Tm}$  etc[16], [102]. An average size of 7 nm of  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  co-doped  $\text{NaYF}_4$  nanocrystals were being synthesized at elevated temperature by Schafer group [102].

For synthesizing UCNPs precursor's properties also play a significant role in controlling size, shape and morphology.  $\text{NaYF}_4$  nanocrystals co-doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  can be synthesized in the presence of precursors like-  $\text{Y}_2(\text{CO}_3)_3$ ,  $\text{Yb}_2(\text{CO}_3)_3$ ,  $\text{Er}_2(\text{CO}_3)_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{F}$  as they can produce nanocrystals even at room temperature or at very low temperature having hexagonal phase ( $\beta$ -phase) giving better luminescence and high yield. This is one of the noteworthy advantages of these precursors providing a novel method of synthesis procedures at nanoscale production. Such novel synthesis method is based on the reaction of metal carbonates with Ammonium fluoride and synthesized in organic solvents in the range of temperature 20–280°C. After decomposing of metal precursors pure, nanosized  $\text{NaYF}_4$  nanocrystals co-doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  were formed having high yielded particles which are well separated, and they contribute to broad size distribution (particle size~ 4-10 nm). Thus, the transparent solution of these resulted nanoparticles exhibited visible Upconversion emission on 978 nm of wave excitation. After that novel synthesis all the diffraction peaks appeared by XRD assign to hexagonal phases and no cubic phases are assigned, that means here as all the phases belong to hexagonal phase, so luminescence efficiency which is our desirable property becomes high. Cubic phase of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  co-doped  $\text{NaYF}_4$  nanocrystals can be produced at elevated temperature (250°C). All these reactions were done in pure oleylamine which can be replaced with oleic acid - oleylamine mixtures to discontinue the cubic phases formed in reaction. With the above mentioned precursors under optimized

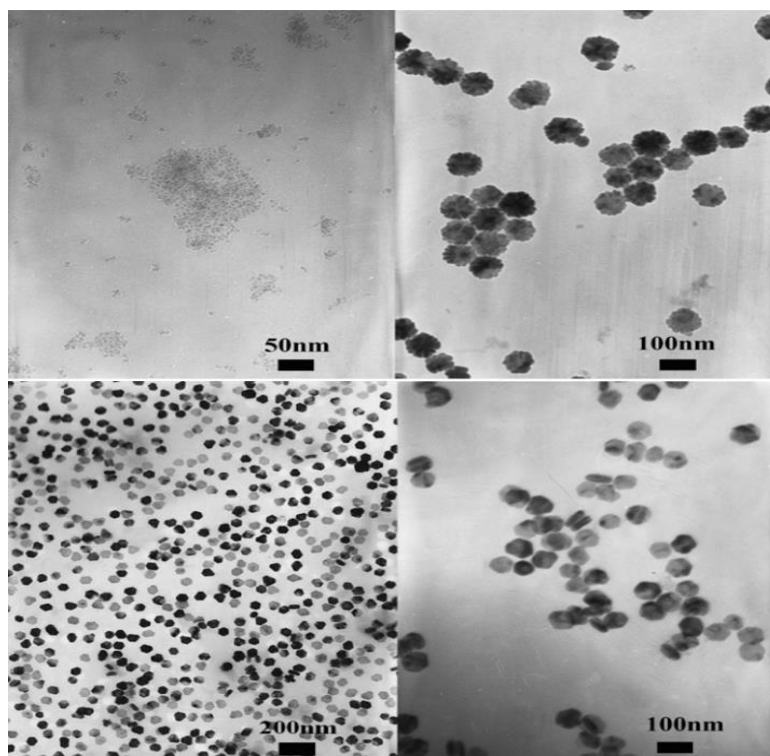
conditions 7 nm sized particles (estimated as an average particle size) were formed having 84% yields [102].  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  ions coupled in hexagonal phase  $\text{NaYF}_4$  matrix provides highest up conversion efficiency [3], [98]. Proper heat treatment is an important factor to increase the luminescence efficiency.

Thus, solid-state-reaction procedure is another way to form nanoscale hexagonal  $\text{NaYF}_4$  powder with releasing ammonia at room temperature grinding dry powders (such as  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{F}$ , and RE carbonates powders). However, owing to the presence of higher percentage of  $\alpha$ -phases and other phases/ impurities rather those  $\beta$ - phases in the as-synthesized sample this procedure carries less importance compared to the others mentioned above. Not only that but also it requires high reaction temperature ( $\sim 300^\circ\text{C}$  or above) during synthesizing Upconversion nanocrystals.

Ionothermal synthesis is the procedure where ionic liquids are used as reaction media in thermal reactions and water-soluble hexagonal phased  $\text{NaYF}_4$ :  $\text{Yb}^{3+}$ ;  $\text{Er}^{3+}/\text{Tm}^{3+}$  nanoparticles are formed with. Mostly this procedure occurs in a molecular solvent [103], [104].

A conventional strategy for synthesis of nanocrystals is based on a simple and agreeable methodology, known as Liquid solid solution process (LSS) which provides a variation of building blocks for assembling materials in nanotechnology. To obtain high quality nanocrystals, basically noble metals have been chosen for achieving good uniformity, smooth surface and self-assembly. Three phases are developed during this process - solid phase, liquid phase and solution phase. It is possible to obtain uniform noble metal nanocrystals by the moderation (reduction) of noble metal ions from interfaces of solid, liquid and solutions at various classified temperature. Here, metal-linoleate acts as solid phase, ethanol- linoleic acid acts as liquid phase and water- ethanol solution with noble metal ions serves as solution phase. To generate liquid and solution phase ethanol is a common quantity. The greatest advantage of LSS process is to produce nanocrystals having various properties such as, magnetic, semiconducting, fluorescence, dielectric and applications in solid state lasers, luminescent probes and sensors [105].

We can divide the whole LSS process into two sections, (i) phase transfer process and (ii) phase separation process. In phase transfer process, the aqueous solution with noble metal salt conjugate with ethanol, which is also in a liquid form and produce water- ethanol solution containing noble metal ions. Again, phase transformation based on ion exchange occurs between sodium linoleate and the water- ethanol solution accommodating noble metal ions resulting in noble metal linoleate and finally sodium ions enter into the aqueous phase.



**Figure 1.3.3: TEM images of NaYF<sub>4</sub>:Yb, Er UCNPs obtained at different reaction temperatures. Reported with permission. Copyright: Chemistry of Materials publication**

At certain selected temperature, ethanol in both phases (liquid phase and solution phase) alleviates noble metal ions at the interfaces of solid liquid and solid – solution phases [105]. Here the only remaining quantity which not reacting with other chemicals is the linoleic acid, which is absorbed on the noble metal – nanocrystal surface further with the reduction process

(reduction of the noble metal ions). As a result, alkyl chains are developed outside the noble – metal surface enabling them to acquire hydrophobic surfaces. In LSS process phase separation occurs spontaneously owing to the weight of nanocrystals as well as incompatibility between their hydrophobic surfaces and hydrophilic surroundings.

In figure 1.3.3, TEM micrographs of  $\beta$ - NaYF<sub>4</sub>:Yb, Er nanoplates [96] prepared by liquid-solid dual phase - approach are shown.

## **1.4 Few recently developed synthetic strategies**

Now in the subsequent section some of the recently developed synthetic strategies for UCNPs and their special investigations have been summarized.

### **1.4.1 Microwave assisted synthesis**

There are two leading mechanisms, Dipole rotation and ionic conduction, which determine the potentiality of a material for absorbing microwave radiation and transmuting it into heat. Though mostly, microwave assisted synthesis was used in organic synthesis but nowadays to prepare monodispersed Upconverting nanocrystals [106]–[109] this method is being used. Some advantages are there behind using such method, they are

- a) Convenient and reproducible method which allows preparing highly luminescent, small monodispersed nanocrystals [108].
- b) Rapid reaction takes very less time to complete the reaction and to form luminescent nanocrystals.
- c) Provides particles having different required sizes and shapes.

d) Hence, the polar reactants (accompanied by high microwave extinction coefficient) are excited by direct absorption of microwaves and as a result the activation energy reduces, consequently reaction rate enhances. As outcome, lower temperature is required to perform the reactions, therefore, additional temperature in inhomogeneities is being eliminated and the leading experimental parameters (time, temperature, pressure) become easier.

e) Growth and nucleation of resulting nanocrystals in such synthesis procedure can be distinctly described with clear explanation. Hence, growth and nucleation of nanocrystals occur in three phases, in first phase, slowly the reactant concentration increases and finally exceeds solubility, in second phase, reactant concentration extends the critical limit of super saturation, therefore, rapid nucleation is obtained and eventually this nucleation burst, reactant concentration reduces to the depletion of the solute for the growth of generated nuclei and here nucleation stage ends. In the third phase, gradually nuclei grow. Such processes follow the LaMer Mechanism. In such way, the whole reaction can be managed favorably and the resulting nanocrystals exhibit excellent monodispersity and crystallinity due to polar reactants, high microwave extinction coefficient.

#### **1.4.2 Photopolymerization**

Using this strategy it is possible to induce different monomers with different desired functional properties (such as- Hydrophobic or hydrophilic, charged or neutral, chemically active or inactive) within up converting nanocrystals by coating them with thin polymer shells known as photopolymerization which utilizes internal UV or emitting visible light from them on NIR excitation. This is a simple, generic and straightforward and versatile approach to functionalize, conjugate, protect and make Upconverting nanoparticles bio-compatible [110].

Utilization of NIR excitation in photo polymerization provides special advantages like, less probability of occurring photo damage to living cells owing to its high tissue penetration depth, ability (due to its higher wavelength ) to avoid photo bleaching, weak chemical stability as such difficulties arise with excitation having lower wavelength [111], [112]. With photo polymerization, upconverting nanocrystals draw some disadvantage while using in biological media, as they are hydrophobic in nature and non- dispersible in nature. Therefore, after photo polymerization also their surfaces are needed to be modified and functionalized in a precisely controlled manner [113].

#### **1.4.3 Advanced and recent Synthetic strategies in UCNPs with various advanced applications**

Recently, unifying core and shell material became most attractive synthetic strategy yielding high quality and high sensitivity involving energy transfer process between  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  ions [114]. There exists a twisted relationship between Upconversion efficiency and lattice geometry providing a strategy for designing the quantum efficiency of any lanthanide upconverter. This strategy has been published in literature in present-day [115]. The chitosan – conjugation is the another method to increase the cell viability of Upconverting nanocrystals in human breast cancer cells , in such approach Upconverting nanocrystals exhibit bright Upconversion fluorescence with controlled size and shape on 974 nm excitation [116]. Upconversion nanoparticles can also be served as luminescent nanothermometers over a wide temperature range and such nanothermometers can be processed by affiliation of liquid-solid solution hydrothermal strategy and thermal decomposition strategy and become excellent temperature sensor [117]. Lanthanide doped Upconversion nanocomposites (such as-  $\text{Ln}^{3+}$  doped  $\text{BiPO}_4/\text{BiVO}_4$  nanocomposites) can also be used for photocatalysis applications. Lanthanides, (ex.  $\text{Tm}^{3+}$ ) emit strong blue spectra, which are transferred  $\text{BiVO}_4$  resulting formation of excitations, which produces reactive oxygen species. In literature survey, it has been suggested that upon NIR and solar irradiation photocatalysis activity of such resulting

Upconverting nanocomposites are more advantageous than the reported general nanocomposite photocatalysts. In recent past years, few advanced applications of UCNPs have been established, such as, a multifunctional nanocluster having dual compositions of gold nanorod (AuNR) and UCNPs showed applications in imaging of cancer cells and treatment. In neuroscience and engineering, stimulating deep brain neurons is an important desire. Molecularly tailored UCNPs (dendritic) have been served as less invasive optogenetic actuators to stimulate deep brain neurons [118]. UCNPs based theranostic system is very useful for multi-drug resistance reversing ability for chemotherapy [119]. A UCNP based system:  $\text{LiYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}@\text{SiO}_2$  coated with chitosan (CH) hydrogel has become an excellent theranostic platform by controlling drug-delivery and deep-tissue-imaging for several important applications- tissue engineering, bio-mapping and cellular imaging [120]. Highly specific tumour-imaging can be exhibited by the conjugate forms of Upconversion-nanoprobes with cancer cell (CC) membrane, such combined form (CC-UCNPs) represents novel materials presenting attractive class of advanced materials [121].

#### **1.4.4 Investigation of phase transformation and morphology tuning in UCNPs**

Phase and morphology of UCNPs can be tuned by using proper dopant ions. Zhang's group and Kal's group have been already depicted the crystal structure of such upconverting nanocrystals through  $\text{K}^+$  ions co doping [122] and there are various literature reported on the different morphologies and phases of the resulting nanocrystals [96], [123]–[125]. Phase transformation and morphology both are dependent on several experimental parameters, such as reactant's concentrations, reaction time and reaction temperature. Concentration of dopants can also play a significant role on phase transformation. For example, different concentrations of  $\text{K}^+$  ion dopants in  $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$  nanocrystals display different XRD peaks. It has been reported that upto a certain limit (60 mol %) of such dopant concentration hexagonal  $\text{NaYF}_4$  nanocrystals become dominant phase but beyond that limitation (when exceed 60 mol %: around 80 mol % to 100 mol %)  $\text{K}^+$  ions replace  $\text{Na}^+$  ions and form hexagonal  $\text{KYF}_4$

nanoparticles that mean phase transformation takes place [122]. The reason behind that phase transformation is the imbalance of the intrinsic crystal structure.  $K^+$  ions only settle in the substitution position of  $Na^+$  ions and when number of occupying  $K^+$  ions becomes large compared to  $Na^+$  ions (at that moment  $Na^+$  ions are too few), hexagonal  $KYF_4$  appears having poor crystallinity.

Now, how the morphology of UCNPs ( $NaYF_4:Yb^{3+},Er^{3+}$ ) can be tuned with tuning concentration of dopant ions ( $K^+$  ions), is shown in the table 1.4.1 below:

**Table 1.4.1: Tunable morphology of UCNPs with controlling  $K^+$  ions**

| <b>Concentration of <math>K^+</math> ions (in mol %)</b> | <b>Morphology of resulting nanocrystals</b>                             | <b>Diameter of the resulting particles</b> |
|----------------------------------------------------------|-------------------------------------------------------------------------|--------------------------------------------|
| 0                                                        | Spherical ( $NaYF_4$ )                                                  | 26 nm                                      |
| 20                                                       | Regular hexagonal cross section(plate-like; uniform in size; $NaYF_4$ ) | -                                          |
| 40                                                       | Rectangular-like cross section( $NaYF_4$ )                              | -                                          |
| 80-100                                                   | Spherical hexagonal( $KYF_4$ )                                          | 20 m                                       |

#### 1.4.5 Mechanistic Investigation of photon Upconversion

It is known, in most of the cases that the lanthanide doped upconverting materials (ex:  $NaYF_4:Yb^{3+}, Er^{3+}$ ) need 980 nm excitation. But this event creates problem which became a daunting challenge nowadays as absorption band of  $Yb^{3+}$  (980 nm), which acts as dopant in host lattice ( $NaYF_4$ ), dangles with absorption band of water molecules used in the biological sample. Therefore, under 980 nm excitation overexposure of biological species results in cell death and tissue damage due to overheating issues. To overcome such drawback 980 nm laser

excitation can be replaced by 800 nm laser excitation occurring low absorption coefficients and it is possible through use of  $\text{Nd}^{3+}$  dopant ions as sensitizer due to their favorable characteristics (As their sharp absorption bands are centered around 800 nm) [126]

## **1.5 Biological applications of UCNPs based on their immobilization to assemblies:**

For several biological applications, surface modification of UCNPs plays an important part for upgrading their photostability and to attach with bio-molecules. Normally, UCNPs bear a good portion of surface dopant ions. Now presence of weakly bound impurities on surface and ligands can diminish the luminescence of dopant ions due to the creation of high energy oscillations. On the other side, the excitation energy of interior ions can be dissipated non-radiatively due to their transferred energy towards the crystal- surface. As a result, the crystal field - strength decreases and finally the overall UC luminescence intensity reduces abruptly. To overcome this drawback, surface modification (surface passivation and surface functionalization) is required. By surface passivation, all the dopant ions can be confined in an interior core and therefore can dominate the energy transfer towards crystal-surface. An Upconversion luminescence enhancement of about 30 times was successfully carried out by one research group with 1.5 nm thick  $\text{NaYF}_4$  shell on 8nm sized  $\text{NaYF}_4\text{:Yb/Tm}$  nanocrystals [127]. By varying the thickness of the shell, UC luminescence efficiency can be well tuned and by several research groups [33], [98], [128], [129] this process has been successfully explained by immobilizing the nanocrystals (UCNPs) inside a coated shell. Besides, surface passivation, surface functionalization is also an important part to use those UCNPs in biomedical and biodetection. Hence, by ligand exchange technique  $\text{NaYF}_4\text{:Yb/Er}$  nanoparticles can be made water soluble by utilizing bi-functional organic molecules which replaced amine ligands and modified the crystal surfaces as water-soluble carboxyl functionalised surface[15].

Moreover, the immobilization concept of UCNPs has been confirmed by their several biological applications via bioconjugate chemistry as these techniques are, while applied to UCNPs, capable of immobilization to bio-assemblies. Based on the immobilization concept, some specific bio-applications of UCNPs are discussed below.

In cells and small animals, the innovative UCNPs have been considered to be promising molecular probes for optical imaging. In 2013, Grebenik et al. group reported UCNP-labeled cancer lesion where the synthesized nanoparticles were capped with amphiphilic polymer. Further, mini-antibodies (scFv4D5) were attached onto UCNPs for allowing their specific binding to the human cells. As a result, the UCNP based biocomplexes showed high specific immobilization on human breast adenocarcinoma cells SK-BR-3 [130]

In 2017, Shikha et al. group developed a UCNPs based multiplexed detection system to encode PEGDA microbeads and to label antibodies. Hence, the multicolour codes were produced by mixing green and red emissions from UCNPs whereas its blue emissions were used to label antibody. By immobilizing probe antibodies on red-UCNPs and anti-human C reactive protein (hCRP) on green UCNPs, specific capturing of human serum albumin (HAS) protein and multiplexed detection of HCRP and HSA proteins were done, respectively [131].

RGDS and TAT conjugated  $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ ,  $\text{SiO}_2$  nanoparticles were targeted in HeLa cells by in vitro study where RGDS conjugated probes were confined on cell-plasma membrane for the specific binding between the conjugated peptides and integrins. This application also clearly confirms the immobilization behaviour of UCNPs[132].

In 2016, T sang et al. group proposed a conjugated system of  $\text{BaGdF}_5:\text{Yb}/\text{Er}$  UCNPs and AuNPs to increase the effective detection of limit for target Ebola virus from picomolar level to femtomolar level. The enhancement of this ultrasensitive detection exhibited a great potential for practical application due to the specificity between nanoprobe and Ebola virus oligonucleotides[133].

The bare monodisperse UCNPs were immobilized for developing bio-sensing surface. Further, for developing bio-assays and bio-sensors a high immobilization density for UCNPs

was reported by Doughan et al. group in 2014 and the reported immobilization density was calculated of about  $\sim 1.3 \times 10^{11}$  UCNP  $\text{cm}^{-2}$  where PEA – UCNPs were immobilized on functionalized coverslips [134]

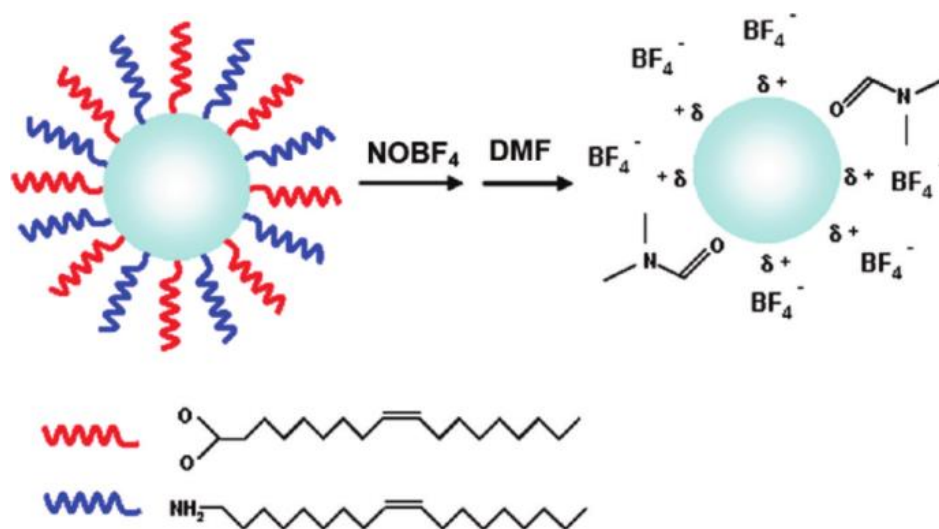
PEG-b-PAAc was immobilized on erbium ion doped  $\text{Y}_2\text{O}_3$  [ $\text{Y}_2\text{O}_3$ : Er] particle - surface to enhance its dispersion and prevent adsorption. Further, co- immobilization of PEG-b-PAAc and BSA occurred due to the protein installation on particle – surface[135].

According to previous report [136] the immobilized photoredox catalyst based on  $\text{NaYF}_4$  nanoparticles was capable for in-vivo applications. The immobilized system successfully performed under 980nm NIR source.

## **1.6 Different Biological applications of UCNPs**

In particular, based on the immobilization strategies, Upconverting nanoparticles have given a huge response in bio-applications. In the applications of cellular and molecular biology, several bio- probes (Green fluorescent protein, (GFP), organic dyes) are used for identification of different bio-molecules, which is an indispensable step. To develop the sensitivity of some technical and analytical devices used in bio-field utilization of such available probes is a crucial step as they improve the efficiency of detection. Still some drawbacks (such as weak photo stability of probes, measuring cell response having instrumental problem with resolution) are there with such bio-probes which limit their biological applications. To overcome such drawbacks nano particles with protein-imaging, nucleic acid-detection with nanodiamonds [137], [138], metallic nanoparticles, dye-doped silica particles have been already discovered. As nanoparticles consist of a large no. of ions, so single particle and single molecule identification is favorable owing to large surface area implanting of different targeting groups at the surface and it can be done comfortably. For more advanced applications recently RE based nanoparticles have been proved to be most optimistic materials [139] due to their especial properties such as long lifetimes, narrow emission lines, high photo stability, low cytotoxicity and simplistic functionalization

procedures which make them highly bio-compatible and recognizable compared with other Nano particles. In magnetic resonance imaging (MRI) due to their high magnetic moment and inoxidant detection applying reverse oxidoreduction process, the requirement of UCNPs is noticeable. In MRI RE ions can be regarded as a powerful contrast agent. To fabricate nanoparticles (e.g. silica particles) [140] as high biocompatible material various chemical properties could be induced by inducing different rare-earth compounds as dopant-agent. Mesoporous silica shell nanocomposites used for bimodal imaging is the best example of such nanoparticles doped with RE compounds.



**Figure 1.6.1: Illustration of ligand-exchange with  $\text{NOBF}_4$ . Reproduced with permission (Dong et al., 2011). Copyright: Journal of the American Chemical Society publication**

Surface modification or surface functionalization and bio-conjugation are crucial steps after synthesis known as post synthesis method before using in the biological field. Every nanoparticle has a certain surface chemistry and specific physical and chemical properties to govern nucleation or growth of resulting particles as well as to control their dispersion in the solvent used. Generally, after synthesis of Upconversion nanoparticles, due to the presence of

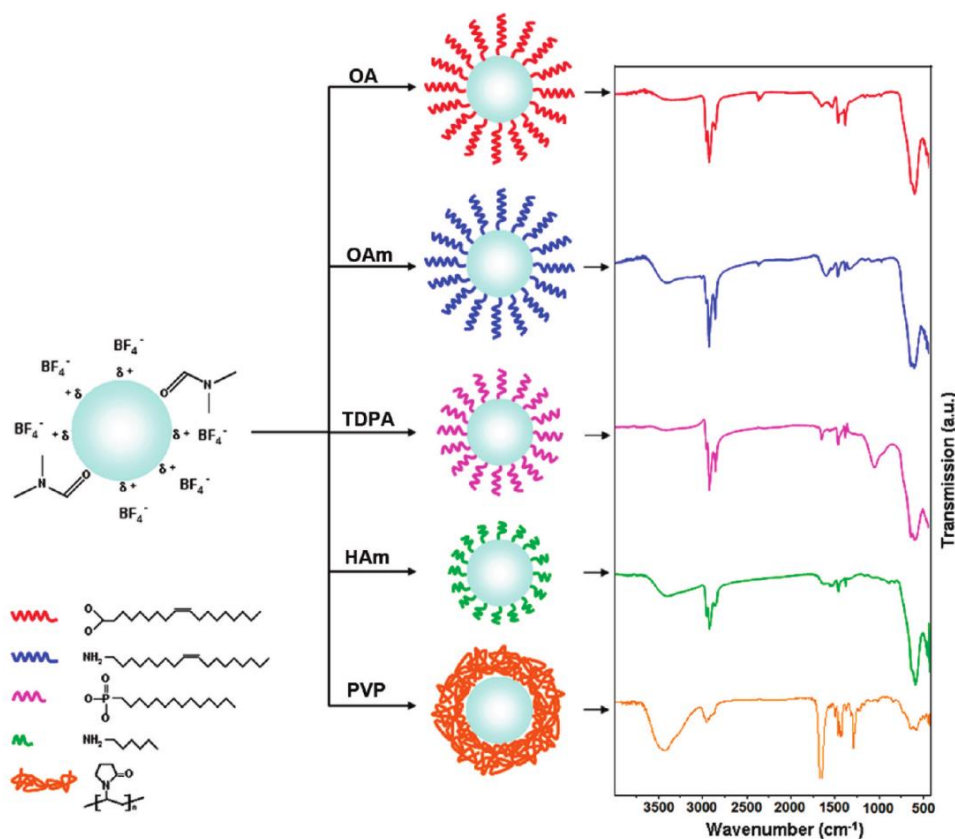
some organic ligands capped with them, they become non-dispersible which are not suitable for Bio-applications. For using in different bio-medical applications Upconversion nanoparticles based bio-probes are fabricated to functionalize their surfaces to ensure good dispersion in biological media and to uncover specific organic or bio organic groups from the particles and to make them appropriate for accurate targeting receptor sites (figure 1.6.1).

Ensuring the stability of hydrophobic nanoparticles in aqueous media is a necessary condition in biological applications and that can be processed by applying diverse functional strategies which are described by following: In Ligand exchange the original ligands are replaced by other molecules Citrate, PVP, PAA, TGA, PEG and finally become stable dispersible in biological media (figure 1.6.2, 1.6.3.) [141], [142].

By direct surface grafting of molecules and polymer encapsulation method, several reactive groups (e.g. amino, thiols etc.) can be attached on the resulting particle –surface [143]. Streptavidin, antibodies are some biomolecules with which nanoparticles can be directly coupled. Because of surface hydroxyl groups acting as a coupling agent with silanes present in the oxide nanoparticles, by silica and organosilane coating functionalization can be done in a quite simple way.

Layer by layer assembly is another propitious method for surface modification, obtaining by sequential adsorption of oppositely charged polyelectrolytes on particle surface. Such sequential adsorption (i.e. sequential deposition of PAA and PAH) has been already observed in literature providing superior mechanical stability and a well ordered NIR to visible Upconversion luminescence. But here some drawbacks which limits its requirement as this method is only applicable for hydrophilic nanocomposites and time-consuming, many washing steps are needed during that assembly. Surface silanization is the most frequently used surface functionalization method requiring the growth of silica shell on Upconversion nanoparticles. The importance of this process is the use of silica as silica is considered to be biocompatible and porosity is easily controllable. The encapsulation of silica layer on UCNPs is still under investigation to modify the difficulties (such as , most of the reagents used are toxic in nature, therefore before starting that encapsulating process they should be detached

carefully) introducing by silica layer and other reagents used in such encapsulating process. If we desire to use silica encapsulation in FRET- biosensors, the increasing shape and size of the resulting particles will create difficulties during experiment. To suppress those difficulties two approaches are useful, one is Stober method and other one is reverse microemulsion route.



**Figure 1.6.2: Illustration of secondary ligand-exchange exhibiting surface functionalization of  $\text{BF}_4^-$  - modified  $\text{Fe}_3\text{O}_4$  nanocrystals with several capping molecules and their corresponding FTIR spectra. Reproduced with permission (Dong et al., 2011). Copyright: Journal of the American Chemical Society publication**

Although controlling that Stober method is quite difficult and takes long time, thus it is straightforward and fruitful path in the presence of ethanol and ammonia, whereas reverse micro emulsion route can be controlled in the presence of homogeneous mixture of water, oil,

surfactant and TEOS to dominate the increasing thickness, size and shape of the additional silica layer. One user-friendly surface modification for providing hydrophilic nanoparticles as well as hydrophobic layer for loading hydrophobic molecules (Drug, Dyes) is the Host-Guest Self-assembly method which has a lot of advantages over the other methods due to its simplicity and efficiency. As this procedure is very fast, over 95% of nanoparticles can be transferred to water using reagents [144].

We've already discussed that by proper surface modification it is possible to affix various functional groups with UCNPs, like- carboxyl, amine, thiol groups. After such functionalization, these UCNPs with several attached groups can be decorated with various biomolecules which can contribute bio-identification of other targeted cells. There are diverse approaches of bio-conjugation. Among these the greatest advantageous method is Direct Physisorption. This method occurs via non covalent force of biomolecules. The activity of proteins and quantum yield of resulting nanoparticles remain unchanged after that bio-conjugation. Assisted Physisorption is of other crucial importance in Bio-conjugation and uses pre-bound molecules and occurs by non-covalent coupling of two molecules. This is an essential method in bio-specificity and bio-sensitivity due to the proper orientation of molecules. By direct chemical coupling of bio-molecules also bio-conjugation can be induced in UCNPs. But this method cannot be controlled easily as other complex processes such as gel electrophoresis is required for separation after completion of this process. In UCNPs' surface modification with biotin-protein bond (streptavidin-coupling) can be useful for various biomedical application, which is the strongest and most stable non-covalent interaction.

A general overview on UCNPs- applications is highlighted below.

### **1.6.1 DNA and Protein detection**

It has become a great challenge for application of RE based nanoparticles for DNA and protein detection. Implementation of such nanoparticles in DNA detection is based on two

strategies, DNA sensitive nanoparticles and DNA fragments nanoparticles. Here we are describing one by one.

In case of the first approach, DNA concentration can be computed using fluorescent Upconversion nanoparticles [145] which can be comparable to conventional measurement executed by spectrophotometer. As per optical properties we already know that fluorescence property UCNPs make them valuable for their applications. Now due to some specific dopant ions (such as:  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}$  dopants in  $\text{LaF}_3$ , fluorescence occur due to  $\text{Tb}^{3+}$  dopant ions) and their transitions in energy levels the fluorescence of Upconversion nanoparticles become very prominent and in the presence of DNA the amount of fluorescence can be quenched by the generating generation of hydrogen bonds between DNA and nanoparticle. As a result, the energy can be transferred from excited dopant ions ( $\text{Tb}^{3+}$  in the given example above) to DNA. Finally, it is possible to quantify DNA concentration by determining the corresponding fluorescence intensity. In the second approach, to study mRNA pattern, DNA microarrays are used extensively for which there are two requirements, one for hybridization of probe DNA strands and other for labeling target DNA fluorescently. In such technology, also fluorescent intensity quantifies the DNA fragments in each probe. Later, other advantageous technology comparable to the depicted one, reported in literature according to which for labeling, target DNA is combined with UCNPs (for ex.  $\text{Y}_2\text{O}_3$ : Yb, Er) and finally it is possible to measure the concentration of the target DNA. The later one is superior technology than the former for determining DNA concentration, as the former technology weakly express mRNA.

UCNPs can also be used for diagnosis diseases such as  $\text{Fe}_3\text{O}_4/\text{Gd}_2\text{O}_3$ : Eu nanoparticles where  $\text{Fe}_3\text{O}_4$  construct the magnetite core and  $\text{Gd}_2\text{O}_3$  constructs the shell of the nanoparticles and the dopant ion  $\text{Eu}^{3+}$  make the particle fluorescent by transferring energy. Now, it is known, detection of single nucleotide polymorphisms (SNPs) is very significant phenomenon for recognition of various diseases like polycystic kidney disease (PKD) by using Reverse Transcription Polymerase Chain Reaction (RT-PCR) but due to some shortcoming vis a vis time consuming and expensive, it cannot be applied in the biomedical field. In the present

days, to solve these problems, successfully UCNPs have been introduced to detect SNPs [146]. In that approach, rare-earth based nanoparticles are used in such a systematic manner, that they can combine both magnetism and fluorescence properties to provide a strong and effective analysis.

Europium doped gadolinium oxide nanoparticles can also be used for detection of protein micro patterns for coupling with antibodies rather than organic dyes. Such rare-earth based nanoparticles with organic cores have also been successfully utilized in immunoassays. As a result sensitivity of the whole complex can be improved in the presence of rare-earth based UCPN nanoparticles.

### **1.6.2 Fluorescent Resonant Energy Transfer (FRET)**

FRET has wide applications (among which protein-protein interaction is the most significant phenomenon with the usage of FRET) in Biomedical-field using other materials. For protein – protein interaction, one protein (labeled with fluorophore) acts as donor and other one acts as acceptor (labeled with fluorophore) using that fluorescence energy transfer method according to which an efficient energy is being transferred from donor to acceptor and as outcome detection of fluorescence become possible providing the basic principle of FRET process. If FRET can be done in the presence of lanthanide systems, then easily such nanoparticles can be served as donors, which gives some effective and favored conditions like prevention from direct excitation, limitations in overlapping spectra and their easy separation, long lifetimes of excited state and less probability of photo bleaching and there are certain reasons why lanthanide nanoparticles were taken in FRET experiment. Hence the lanthanide systems with the large stokes shift permits excitation having shorter wavelength than the absorption by acceptor to prevent direct excitation and UCNPs with large anti-stokes shift permits excitation at much higher wavelength than the emission by acceptor to get a clean detection from FRET. Secondly, due to narrow emission spectrum occurred by lanthanide nanoparticles, there is a very less chance of overlapping between them and acceptor emission-

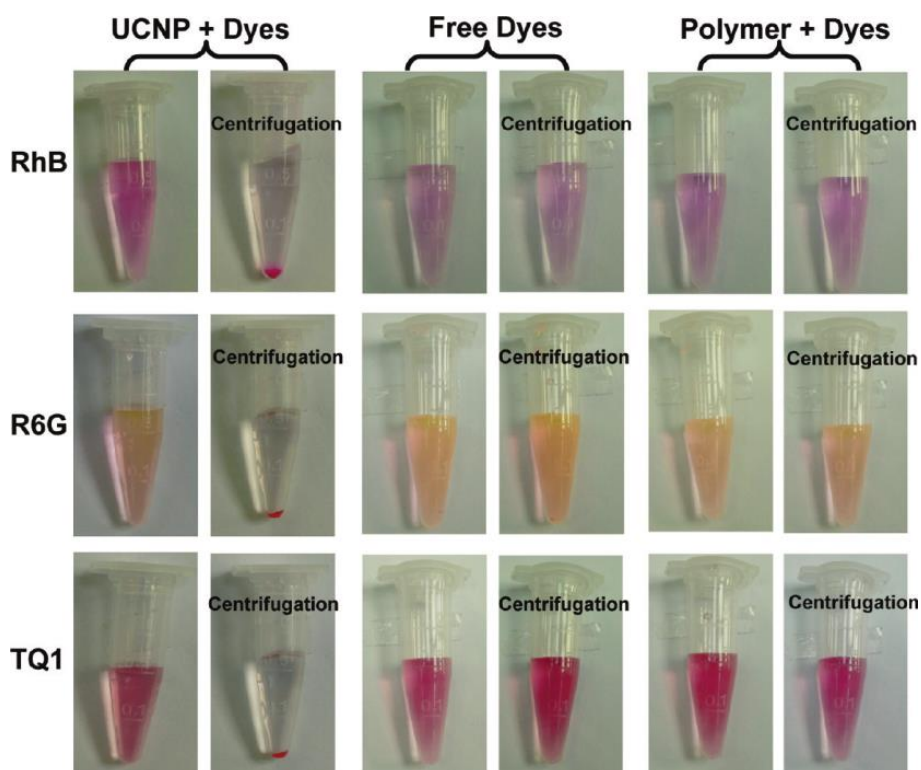
spectrum. Thirdly, as lanthanide systems provide excited states having long lifetime, so conducts acceptor emission with longer time and as a result separation in time-resolved experiments occurs easily. Utilizing that longer-scale phenomenon, it is possible to apply quantum dots as acceptors in FRET applications.

Advantages of Upconversion nanoparticles as donors in FRET application make them unique in biomedical applications. Most of the Upconverting nanoparticles are co-doped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  and gives remarkable fluorescence, which make them an excellent donors having interesting potential in FRET applications. Protein detection with the help of nanoparticles is possible by coating (ex. of such coating, agent-streptavidin), mixing (ex. of such mixing, agent-biotinylated protein) and labeling (ex. of such labeling, compound-fluorescent acceptor) in a precisely controlled manner so that after IR excitation of donors, a clear detection of fluorescence becomes possible.

### **1.6.3 In vivo and in vitro biomedical application**

Recently, lanthanide doped UCNPs have gathered much attention in Biomedicine .In 2012, Liang Cheng et al. showed in vivo imaging of UCNPs in his experiment [147].Auto fluorescence of the UCL imaging with long exposure time allows in vivo detection of UCNPs. UCL emission spectra of different nanoparticles can be controlled with our requirement in biological systems by altering the concentration of the lanthanide dopant ions used during synthesis and this process is essential in multicolour vivo UCL imaging with organic dyes through hydrophobic force (figure 1.6.3) [148]. In tumour diagnosis UCL imaging plays significant role by tumour targeted molecular imaging using UCNP-based nanoprobe. Basically, for synthesis of such nanoprobe conjugating polymer coated UCNPs are used, the aim of which is to bind different cancer cells having high specificity explore a new challenge in future studies and experiments. UCNPs have also been successfully synthesized to utilize in vitro applications such as labeling and tracking rabbit bone marrow

mesenchymal stem cells (rBMSCs) [149]. In 2008, both in-vivo and in-vitro studies were performed using aqueous dispersible rare-earth-ion ( $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$ ) co-doped fluoride ( $\text{NaYF}_4$ ) nanocrystals, where Upconversion process provided deeper penetration into biological specimen resulting high contrast optical imaging [150]. In 2011, in vitro and in vivo imaging was implemented by utilizing 915 nm LASER excited  $\text{NaYbF}_4$  UCNPs co-doped with  $\text{Tm}^{3+}/\text{Er}^{3+}/\text{Ho}^{3+}$ -rare-earth elements to avoid overheating irradiation caused by 980 nm laser excitation source.



**Figure 1.6.3: UCNPs/dye – images captured while centrifuged (before/after). UCNPs and dye molecules appeared as precipitate by centrifugation force while supernatant part appeared as clear colourless solutions in containers. Precipitation was not observed while centrifugation occurred with free dye molecules or PEG-PMHC<sub>18</sub>+dye mixtures. These images indicated that UCNPs- surface adsorbed three types of dye molecules rather than their encapsulation in UCNPs-dye complexes by amphiphilic PEG-PMHC<sub>18</sub> polymer. Reproduced with permission (Cheng et al., 2011). Copyright: The Journal of Physical Chemistry C publication**

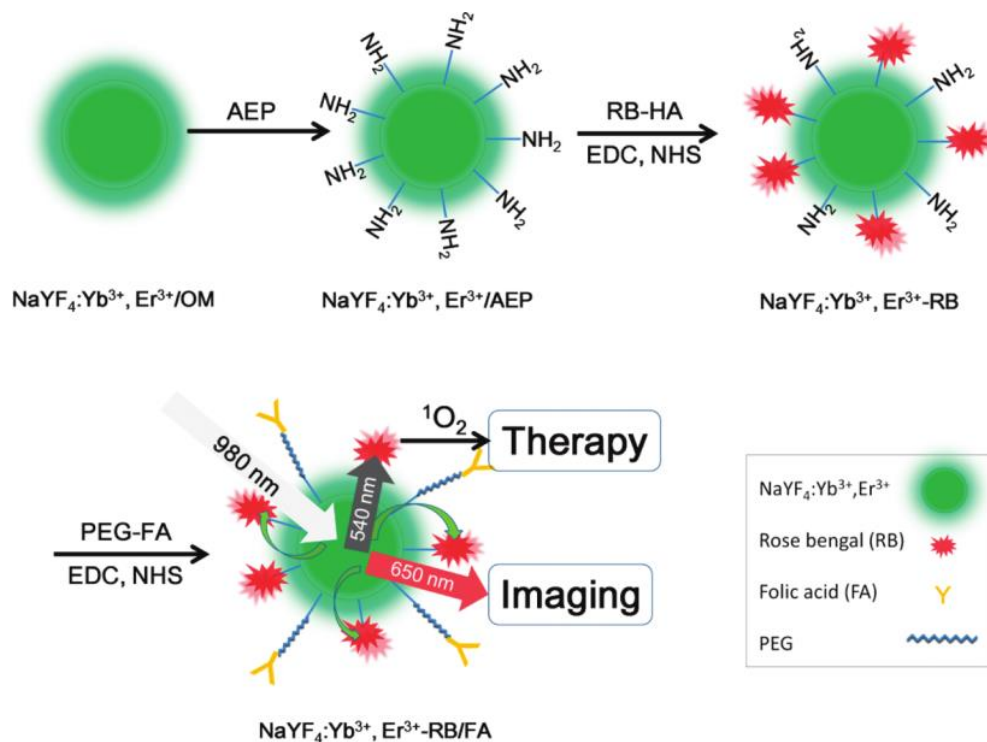
Hence the experimental results were successfully investigated and showed very high contrast Upconversion bio-imaging and a successful performance for in vivo imaging where highly stable UCNPs encapsulated with DSPE-mPEG-5000 were injected into mice [151]. For delivering in vitro and in vivo operations caged UCNPs are being served as excellent platforms to improve targets along with reduction of side effects from chemotherapy by using them as NIR-triggered targets [152].

To overcome the drawbacks of single imaging approach, nowadays the multimodal imaging has gained enormous recognition in biomedical applications. There are several approaches [153]–[155] to progress UCNPs based nanoprobe for multimodal bio-imaging. UCNPs as well as their nanocomposites can be utilized to fabricate such multimodal imaging bio-probes. Also in the field of cell labeling and in vivo tracking, UCNPs are sensible enough. Recently, investigation of mesenchymal stem cells (MSCs) has been started owing to their ability of recognition various types of cells (e.g., bone) under certain circumstances in various potential applications in bio field such as in immunotherapy and gene therapy.

#### **1.6.4 Medicinal and remedial applications**

In present- days, UCNPs and their composites can be considered as therapeutic agent in cancer treatment, drug gene delivery and for photodynamic therapy due to their various unique properties and functions as well as imaging capability. For imaging and therapy, chemotherapy drug molecules could be delivered with loading of UCNPs .For drug releasing system, polymer coated UCNPs can also be used. For treatment of various gene-related diseases, gene therapy with gene encoding DNA or RNA has become a challenging matter. UV light emitted from UCNPs activates definite gene expression by operating DNA and RNA, though depth of penetration. The therapeutic efficiency is very high in case of UCNPs with NIR excitation compared with UCNPs with UV light and such PDT based on UCNPs

exhibited greater potential in treatment of cancers as well as suppression of the size of large internal tumours.



**Figure 1.6.4: Covalent conjugation of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> UCNPs, photosensitizer (RB), target molecule (FA). Reproduced with permission (Liu et al., 2012). Copyright: ACS Nano publication**

To treat cancer diseases Photodynamic Therapy (PDT) is a non-invasive and effective medical method which uses photo sensitizers (PDT drugs) and light irradiation and they interact with molecular oxygen. There are several approaches to originate PDT reagents like, silica encapsulation, polymer encapsulation, and hydrophobic interaction. At first photosensitizers are activated with light and as a result cytotoxic reactive oxygen species are formed and persuade required cell death [156]. Assembly of oxygen molecules are influenced by the energy transfer process from excited UCNPs relying on the spectral overlapping of donor and acceptor impurities in host lattice. There are two factors that quantify

photodynamic therapy, one is high energy transfer efficiency and the other is large production of singlet oxygen and these two phenomenons are related with high stability of originally loaded photo sensitizers in UCNPs. For good energy transfer process non- covalent form of UCNPs-PS is not ideal as this provides low loading efficiency and finally small production of singlet oxygen. For that a covalent conjugating of UCNPs ( $\text{NaYF}_4, \text{Yb}^{3+}, \text{Er}^{3+}$ ), photosensitizer and target molecule strategy can be adopted. For singlet oxygen and high fluorescence intensity production a multifunctional Upconversion nanoplatfrom has been already expanded on the basis of a particular energy- transfer from UCNPs to photosensitizer for synchronous imaging and therapy (figure 1.6.4) [157]. The therapeutic consequences of UCNPs-PS compound for animal studies and cellular level have been already reported[156].It has been reported in literature that for in vitro cancer cell destroying, mesoporous silica coated UCNPs-PS combination shows an interesting and encouraging result [158]. Gu's group has revealed the uses of UCNPs-PS nanocomplexes in the field of in vivo PDT [159]. For in vitro and in vivo tracking UCNPs have been used to designate stem cells by different groups [160].

Superlattices arrangement can be found in crystalline nanoparticles by synthesizing them in a controlled way with a few reaction parameters (in terms differ the interactions between nanoparticles from their bulk materials) which can result a well-defined geometries between the synthesized nanoparticles with improving their several properties such as conductivity, mechanical properties, optical properties, plasmonic properties, etc. depending on its order of packing/arrangement compared to its bulk[161]–[165].On the other hands, self-assembly itself is an activity between nanoparticles or nano-building blocks to assemble them in a more ordered fashion without any external intercession in between synthesis procedure [166]–[168]. However, the combined strategy i.e. self-assembled superlattices would influence their properties [169], [170]. Using interfacial self-assembly approach different interesting geometrical features can be introduced with different length scales for using in different applications and nice distributions of few

ordered structures/patterns have been described in detail (e.g. Honeycomb structures, coffee rings, nanoparticles-superlattices) in a previous literature[171].

This dissertation introduces few interesting self-assembled nano-blocks which have drawn our attention due to their influenced optical properties and assembly over multiple nanoscales. Different applications of self-assembled superlattices (SAMSs) in different nanoparticles are described as following:

As we know, self-assembly between nanoparticles have drawn our attention because of their applications in a large area, including medicinal treatments. Recently, liquid crystals along with nanoparticles have provided an ordered arrangement under controlled reaction-parameters. In one recent literature, the authors have reported about their investigations on self-assembled nanoparticles on liquid-crystal droplets [172]. They have revealed that it the nanoparticles sizes and shapes which controlled the adsorption of different features on liquid-crystal nano - droplets (LC-NDs). They have further reported that sometimes, the shapes and patchiness of resulting nanoparticles could be the reason of having their strong indications of emerging properties. Suppose, if one nanoparticle is not capable of exhibiting favorable adsorption on LC-NDs, 100 nanoparticles could be agglomerated on LC-NDs allowing strong emerging properties. Now, the interactions among nanoparticles shapes, sizes and reactive constitutions have taken a dominant role in achieving self-assembly on LC-NDs. Hence, the authors have mentioned about the huge applications of self-assembled nanoparticles in new sensors and in several advanced materials. LbL - type self-assembly has been proposed to assist a better pharmacokinetics and control the releasing of RSV pursuants [173]. For achieving an improved drug delivery and to activate latent HIV, one kind of self-assembled nanoparticles were employed by researchers by loading with panobinostat (PNP-P) [174]. In 2018, by Huang et al. group, the photoluminescence study was examined with self-assembled nanoparticles (1.6-6.2 nm) conjugated with polymeric thin-film and they are believed to be used in optoelectronics applications where they can behave as host materials [175]. Further,

nanostructures growth has been studied by incorporating self-assembled design on nanoparticle-surface. Depending on the surface and solutions interactions and the concentrations of the solutions used the nanostructures - growth was controlled [176]. In 2019, the Liang et. al. group has reported the formations of nanowires comprising self – assembled nanoparticles which exhibited blue-shifting emission profiles, so they declared promising applications of these self-assembled nanowires for violet/blue light emitters[177]. Even further, the self-assembled PTPPS nanoparticles found potential applications in vitro ad in vivo by reducing the cytotoxicity of TP and exhibited an improved method in chemotherapy especially in malignant tumour research [178]. It is well known, for analyzing subcellular and biological targets the fluorescence/luminescence imaging has promoted fluorescent/luminescent probes. By Long et. al. group one strong application of self-assembled nanoparticles was observed, hence the authors have reported that when the self-assembled nanoparticles were associated with bacteria surfaces, the resulted binding provided fluorescence turn-on signal which was capable to record the bacteria-imaging[179]. The antigen delivery by SAM nanoparticles has been reported to be an optimistic platform by Li et al. group[180]. For monitoring volatile organic compounds( i.e. ethanol, acetone) conductometric sensor was assisted with few SAM nanoparticles[181]. Qiu et. al. group showed the importance of SAM structural configurations by incorporating stable SAM microcapsules which was capable of encapsulating red pigments from paprika [182]. SAM-nanoparticles can influence the utility of PEFC membranes [183]. The hetero-grafted macromolecular brushes provided with amphiphilic nature yielded SAM structures which allowed short backbones [184]. By developing cyclodextrin-based nanoparticles meropenem bio-accessibility and stability was enhanced by popielec et al. group [185]. Biodegradable gelatin-based nanoparticles were prepared with sustaining SAM morphologies for treating skin-diseases [186]. For destroying Bacteria, SAM formations of cationic-nanoparticles (appeared from CSM5-K5 chains) played an important role [187]. Bovine serum albumin – dextran conjugated SAM nanoparticles improved cellular antioxidant behavior in Caco-2 cells [188]. Wang et. al. group reported about the formation of microsphere with SAM

nanoparticles whose sizes were adjustable[189].Guar - gum benzoate based SAM nanoparticles were synthesized for enhancing antimicrobial behavior against the water born gram (+)ve and gram (-)ve bacteria[190].Covalent phenyl-boronic acid based SAM nanoparticles were used for boosting tumour therapies by releasing drugs[191].The importance of SAM pattern of core and shell in polymer nano-conjugate has further been revealed by Liu et al. group who showed their applications in PDT therapy[157]. Lipid ECO/SiRNA SAM nanoparticles were developed to resensitize TNBC which is a promising application in cancer therapy [192]. Using facile synthesis approach, SAM nanoparticles were derived from guar - gum propionate ester and those SAM nanoparticles showed antifungal properties [193]. Novel in-situ SAM nanoparticles (ISNPs) were discovered by Guo group for enhancing stability, palatability and bio-accessibility of RTV( ritonavir) ISNPs[194]. By Pham et. al. research group ISNPs were prepared by novel nanotechnology for reducing pill burdens on pediatric patients [195].Formations of self-assembly by using amphiphilic derivatives were incorporated with WP<sub>5</sub> to exhibit strong NIR emissions along with their pH responses and usefulness in living cells for imaging purpose[196]. Again, previously in 2016, Fa et. al. group proposed self-assembly into nanoparticles by using a squaraine fluorescent probe and multi-interactions for detecting serum-albumin and for living-cell imaging purpose[197]. Conglycinin and chitosan based nanoparticles were prepared by self-assembly pattern with high stability and turbidity. These SAM nanoparticles exhibited drug-release operation [198] .Though Zoledronic acid (ZOL) has been proven to be most potent for inducing cell growth but ZOL encapsulated SAM PEGylated nanoparticles has been found to be most robust anticancer representative [199]. The SAM pattern was induced in nanoparticles by engineering with block-copolymer [PLGA-b-PEG NPs] which acted as nanotherapeutic agent [200]. Further, Wang et. al. group studied the interaction between Liver cancer cell and cholesterol amended SAM nanoparticles [201]. Phase - growth was rapidly controlled by using self-assembly on as-synthesized nanoparticles by Chen group [202].In 2014, by AFM study, Mukherjee et. al. group found the activity of Langmuir- Blodgett tri-layers on SAM nanoparticles sustained with clear morphologies [203]. To represent bio-

detection system (immunosensing with free labeling) nanoparticles were assembled into a nanochannel format just like self-assembly pattern [204]. Yan et. al. group developed Tat-Suc-FA SAM nanoparticles for tumour gene treatment [205]. Cellulose SAM nanoparticles were used in bio-medicine especially in drug carrier and in study of controlled releasing behaviour [206]. To strengthen the microwave absorption potentiality, SAM nanoparticles and their morphologies with ample number of interfaces play an important role. Synthesizing these SAM patterns endures significant challenge to us. SAM nano-flower type pattern was exhibited by Li et. al. group in Cobalt monoxide (CoO) nano-configurations which was controlled during synthesis along with Oleic acid and Oleylamine. This type of nanostructure exhibited great potential in enhancing the microwave absorption. Hence the authors reported the high performances of CoO for electromagnetic shielding [207]. Self-assembled system in as-synthesized nanoparticles has already provided a vital role in drug delivery [208] and electrospinning fields owing to their flexible morphologies sustained in large-area [209]. SAM nanoparticles of  $\gamma$ -polyglutamic acid grafted with cholesterol ( $\gamma$ -PGA-graft-CH) were developed by Li et.al. Group for using them as successful carrier of drugs (i.e. hydrophilic drugs) [210]. A novel synthesis method was proposed for producing SAM nanoparticles by using ( $\gamma$ -PGA-Graft-CH) and hence the SAM nanoparticles acted as protein carriers [211]. According to Jhang et.al. group report, self-assembly occurred in certain nanoparticles after synthesizing them from conjugate products and here the resultant SAMNPs showed higher stability with a large zeta-potential value [212]. One review article presented about the application of SAMNPs of 3D nucleic acid as gene therapy by a significant Si-RNA delivery [213]. Antitumor doxorubicin (DOX) drugs were confined in SAMNPs by incorporating  $\pi$ - $\pi$  interactions for drug delivery (specifically antitumor) [214]. The taurocholic acid (TCA) and heparin – docetaxel (DTX) were designed in a coupled form to conjugate with SAMNPs which located the TCA on particle-surface whereas DTX inside core. This conjugate form was capable for cancer treatment approaching with oral delivery [215]. In 2012, on Ag nanoparticles, self-assembly pattern was involved by Meikun Fan for localizing surface plasmon resonance (LSPR) owing to presence of several functional groups attached with self-

assembled configurations. Hence, the author reported a 3-4 times enhanced SERS on multiple self-assembled surfaces[216]. The SAM polymeric nanoparticles have suggested being excellent materials for delivery of anti-inflammatory and antioxidative representatives in atopic dermatitis therapy [217]. The self-arranging capabilities in certain monodisperse nanoparticles provided a modifiable tool for encapsulation and for controlled releasing behaviour of pharmaceutical compositions [218]. ZOL encapsulated SAMNPs were developed for human cancer therapy [219]. Chemically-assisted SAMNPs have been developed in a large scale area for several nanoscale devices (Optical/ Electrical/ Magnetic) and therefore their production has become attractive[220]. Self-assembled carbon-nanotubes or polymer composites were prepared by inducing electric- field interaction[221]. By Salzano group SAM PEGylated Nps were prepared for cancer therapy followed by bisphosphonates - delivery into tumors [222]. Certain SAMNPs conjugated with PECD – cationic polymers were potentially used for gene transfection where those PECD – SAMNPs served as efficient carrier agents[223]. Individually, by Cao group, the SAMNPs of PLLA-PC were produced by solvent evaporation procedure. After analysing their properties, the authors reported their great potentiality in drug-delivery system (specified for hydrophobic drug)[224].The self-assembly was designed in block- copolymer conjugated with nanoparticles for delivering docetaxel to human- tumor cells[225]. The applications of CsB /DNA self-assembled nanoparticles (CsB/DNA NPs) found in gene delivery with influencing transfection efficiency [226]. Few authors reported about the formations of SAM nanocomplexes which were stable and bio-friendly. These nanocomplexes were formulated by incorporating self-assembly pattern of  $\gamma$  PGA and chitosan. Hence, the authors believed their uses in various biomedical applications carrying with 40-285 nm particle diameters [227] . According to one report, the supramolecular networks were assembled spontaneously and showed their efficiencies such as in energy-transfers and MRI. Few adaptive properties were also observed in this self-assembly pattern as mentioned in this report. These adaptive properties direct their biocompatible nature. Hence, the related application-oriented experiments were also depicted in this report [228]. BOXD-T8 derivatives were assembled

into nanoparticles to form self-assembly pattern which showed strong fluorescence [229]. For cancer therapies (like drug delivery/gene delivery/therapy) targeting receptors became important. In an experimental study, SAMNPs were designed for presenting targeting-ligands (u-PAR) which further appeared for observing RME and drug delivery [230]. Previous report also confirmed that SAMNPs remain effective and can act as nucleation representatives for fatty acids with various lengths of its chains. The report described about the seed-mediated nucleation strategies for creating SAM pattern [231]. One group of synthesized SAM materials provided potential ability as chemosensors [232]. The shape-directed SAMNPs were used to design nano and microdevices where the SAMNPs owing to their assembled configurations were able to accommodate various functional additives and this invention was done by Desimone et al. group and was filed for an US patent( United states patent application publication, Pub. No. US 2010/0055459 A1). Stable and biodegradable SAMNPs based on  $\gamma$ -PGA and chitosan were prepared having particle-diameter of about 20-285nm. Here the authors believed on their uses in biomedical as also described in ref 57 [227]. Further, SAMNPs were prepared for tagging specific quantum-dots, the fluorescence intensity of those dots were influenced by tagging them with SAMNPs[233]. By developing SAMNPs, liposomal agents were delivered by linking them with Pal-PLS[234]. The importance of the engineered SAMNPs along with their present applications and advantages were discussed in detail by Dusica Maysinger [235]. The uniform and assembled nanoparticles were used to fabricate flash-memory tool as reported in an article. Hence, the SAM morphology in nanoparticles were occurred by fabricating SAM-Protein lattices (such as chaperonin) arrangement on oxide-layer and afterwards, by trapping the nanocrystals on specified- cavity spaces of SAM-Protein, the SAM pattern was developed externally by annealing –treatment and this invention was filed for US patent (United states patent application publication, Pub. No.WO2006127589 A1).From SAM-polymeric macromolecules, nanoparticles were developed particle-diameter 20-44 nm by Slomkowski et al. research group. Hence, the obtained nanoparticles showed successful drug-release behaviour in a faster-way [236]. Another study revealed about the in-vivo stability of self-aggregated nanoparticles for

possessing lower concentration values [237]. Further, SAMNPs (where gold NPs bind the surface) were used for bio-detection purpose by influencing its sensitivity which depended on the binded-area [238]. By distributing hydrophobic groups of Amphipol A8-35 in an assembled pattern, SAMNPs were developed [239]. Though viral vectors used for gene therapy were efficient, still limitations are there due to deficiency of those systems in therapies. Non-viral vector system appeared to be safer. Therefore, a review has been made by focusing on synthetic and self-assembled non-viral system of nanoparticles and it further exhibited the importance of SAMNPs in gene therapies [240]. Further, Novel SAMNPs were prepared using polycondensation method. Hence the resulted NPs were degraded in water and a narrow particle-size distribution was observed [241]. Ultrasmall SAMNPs of polyNIPAM-BA were also reported which further confirms about their stability in a large scale of temp-range. Here, the formed nanoparticles were useful to design optical nanothermometers [242]. Involving nanoprecipitation method, PTPP-SAMNPs (PTPPSN) was prepared. In both of in-vitro and in-vivo study, they have found an efficient and improved effect while compared with its original prodrug. This experiment is useful for malignant tumour therapies as described in ref 7[178]. To design biomaterials, self-assembly pattern has become an important process, has been confirmed by Paik et al. research group who have reported about 3D  $Zn_3(PO_4)_2$  SAMNPs which has increased the surface-interactions with bio-substances. Hence, the in-vitro study confirms about their uses in bone-tissue engineering [243]. Tat-Suc-FA SAMNPs were used to further improve tumor therapy owing to their enhanced efficiency and specificity in such bio-applications [244]. Other c(RGDfk) conjugated SAMNPs were incorporated for therapies as they used in SiRNA-delivery to target specific gene VEGFR2 [245]. SAMNPs have been developed for facilitating or enhancing few specific properties specially, delivery properties in cells/tissues[246]. HA-SAMNPs were useful for targeting tumors [247]. The improved silver SAMNPs were incorporated in trapping plasmonic light[248]. The DC transport has been appeared with 2D silver SAMNPs[249].Electroluminescence was studied with CdSe SAMNPs [250] To fabricate biosensors , SAM layer formations were prepared with CNT and platinum NPs [251]. For signal

amplification, electrochemical sensors, consisting with SAM monolayers, were used [252]. Electrocatalytic reduction was enhanced by employing SAM layers of copper and nickel substitutes[253].

## 1.7 Conclusions

This review explores recent developments of UCNPs along with a detailed survey and as application part it focuses in bio-fields (imaging and therapy). Though there are tremendous amount of applications and a number of exciting aspects have been reported in literatures since past few years on this field but still many challenges are ahead especially in imaging and therapy for using UCNPs in an advanced way.

With reducing the sizes of UCNPs the quantum yield became lower which limits their use in various nano-probes. Later, several research groups modified the synthesis and production of UCNPs to increase their yield under continuous wave-excitation sources but still future efforts are required to make them useful for enormous number of in-vivo applications. The long term toxicity of RE doped UCNPs is another perturbation. Though, biocompatible coating-based UCNPs ( $\text{NaYF}_4$ ) appeared to be safer to cells (with precise concentrations) compared to bared UCNPs but still other factors like their interactions with immune systems, interference with the reproductive system, whether the toxicity is affecting for next generation applications, that are still not known for which more number of systematic investigations are demanded. The effects of surface functionalization and sizes of UCNPs on in- vivo behaviours are required to improve in reducing certain potential toxicity. Though imaging and therapies based on UCNPs and their different nanocomposites have been revealed in previous literatures, to achieve synergistic therapeutic effects and realize real-time scanning of treatment development an improved design of UCNPs based on novel multifunctional agents are needed further for simultaneous medical diagnosis and cancer treatment.

## **1.8 Motivation of this dissertation:**

It is evident that with reducing the sizes of UCNPs the quantum yield became lower which limits their use in various nano-probes. Later, several research groups modified the synthesis and production of UCNPs to increase their yield under continuous wave-excitation sources. However, still efforts are required to make them useful for enormous number of in-vivo applications specially with unique sizes. The long-term stability and toxicity of rare earth doped UCNPs is another challenge.

Moreover, upconversion enhancement has been an exciting topic for rare earth nanoparticles and nanolumiophores due to their potential uses in several display, electronic and laser devices including several biological applications (bio-imaging). But on all those points, we need to improve the synthesized nanoparticles by incorporating different parameters.

The effects of sizes and morphologies in UCNPs for several applications are required to improve in reducing certain potential toxicity and increasing stability in their colloidal dispersions and also to improve their upconversion efficiency under certain excitation sources. Different sized and structural configurations of UCNPs based on novel synthesis methods by varying different reaction parameters are needed further for improving their spectroscopic properties to enhance upconversion emission so that they could become potential candidates in an additional number of future applications.

Therefore, based on this the following objectives are formulated for this dissertation:

1. Synthesize UCNPs at relatively lower reaction temperatures and times as much as possible with choosing appropriate precursors and always approach a simpler and straightforward method. Control reaction time and reaction temperature to overcome some drawbacks during synthesis (Particle aggregation, enlarged particle size).

2. Enhance up-conversion intensity with incorporating only fluorides and avoiding bromides and chlorides as they are sensitive to moisture and therefore not worthy for bio labeling or imaging.
3. Synthesize high quality UCNPs with a user-friendly method (one-pot chemical approach) to avoid the existence of fluoride reagents in high reaction temperature.
4. Synthesizing UCNPs in different ways (by varying reaction parameters) to achieve controllable shapes, sizes and structures with an efficient UC fluorescence/luminescence.
5. Prepare different sized and structured UCNPs such as UCNPs-hexagonal, UCNPs-Dot, UCNPs-Dendrimers, UCNPs-Superlattices having a sufficient amount of UC emission under NIR excitation sources.
6. Correlate and analyze relevant findings to the spectroscopic properties along with their variations in fluorescence/luminescence by observing their emission spectra under different excitation sources (single laser laser-diode 980nm NIR, Femtosecond laser source 940-990nm NIR).

## **1.9 Arrangement of dissertation:**

The present dissertation has been organized in four chapters, which are given as,

**Chapter 1:** This chapter includes introduction, literature reviews, motivation and objectives of dissertation.

**Chapter 2:** This chapter covers experimental part along with the materials and methods that have been used for synthesis purpose and also the characterization techniques.

**Chapter 3:** The whole result and discussion part is described in chapter 3, which is divided into five parts:

**Part I.** In first part, hexagonal UCNPs (sizes ~200nm) have been synthesized with highest photon upconversion efficiency with 980nm laser diode source (NIR) and Femtosecond-laser source.

**Part II.** In second part, different characterizations and emission properties have been discussed in upconverting nanodots (UCN-dots) which appeared with particle sizes below 5 nm and effectively can generate high intense UV emission while interacts with 140 femtosecond laser pulses.

**Part III.** In third part, a novel synthesis has been introduced for preparing upconverting-nanodendrimers (UCN-Ds) in necklace or chain formations. Their characterizations and emission properties have also been discussed in this part.

**Part IV.** In fourth one, self-assembled superlattice formations of UCNPs (SAM-UCNPs-SL) have been shown with controlling several parameters and further their emission properties (fluorescence, luminescence, photoluminescence) have been investigated along with introducing characterization techniques.

**Chapter 4:** The last chapter will be presenting the summary of the research work including conclusions and future scope.

**References:** At the end of chapter 4 references are listed accordingly.

## **2 EXPERIMENTAL SECTION**

### **2.1 Outcome:**

#### **Patents Filled:**

1. Stable upconversion nanoparticle super- lattice (UCN-SL) & in-situ process for developing thereof; Ref. No./Application No.- 201841037607
2. Stable upconversion nanoparticle dendrimer (UCND) & method of making thereof; Ref. No./Application No.- 201841037609
3. upconversion nanoparticle DOT (UCN – DOT) of size 3.5 nm & its preparation process thereof; Ref. No./Application No.- 201841037608

In this chapter, the materials used to synthesize different UCNPs with controlling several reaction parameters are introduced. The synthesis methods have also been depicted. Different characterization tools to characterize synthesized materials have been discussed in this section with their working principles.

## 2.2 Materials used to synthesize UCNPs:

**Table 2.2.1: Materials used to synthesize UCNPs:**

| No. | Chemicals used                                                        | Purity in percentage | Company source     |
|-----|-----------------------------------------------------------------------|----------------------|--------------------|
| 1.  | Methanol                                                              | 99%                  | FINAR              |
| 2.  | Ethanol                                                               | 99.5%                | Merck              |
| 3.  | Acetone                                                               | 99.5%                | Merck              |
| 4.  | Ammonium Fluoride( $\text{NH}_4\text{F}$ )                            | 97%                  | Kemphasol          |
| 5.  | Sodium Hydroxide( $\text{NaOH}$ )                                     | 97%                  | SDFCL              |
| 6.  | Sulfuric Acid( $\text{H}_2\text{SO}_4$ )                              | 99%                  | Qualigens          |
| 7.  | Potassium Permanganate ( $\text{KMnO}_4$ )                            | 99%                  | SDFCL              |
| 8.  | Cu solution                                                           | 98%                  | Kemphasol          |
| 9.  | $\text{CaCl}_2$                                                       | 98%                  | SDFCL              |
| 10. | Yttrium Chloride salt ( $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ )    | 99%                  | Sigma-Aldrich      |
| 11. | Ytterbium Chloride salt ( $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ ) | 99%                  | Sigma-Aldrich      |
| 12. | Erbium Chloride salt ( $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ )    | 99%                  | Sigma-Aldrich      |
| 13. | Oleic-Acid( $\text{C}_{18}\text{H}_{34}\text{O}_2$ )                  | 63%                  | Qualigens          |
| 14. | Cyclohexane( $\text{C}_6\text{H}_{12}$ )                              | 99.9%                | FINAR              |
| 15. | Inert Gas (Ar gas)                                                    | 98%                  | Sidhi Vinayaka gas |
| 16. | De-ionized water                                                      | -                    | -                  |

## **2.3 Methods for synthesizing UCNPs:**

The synthesis methods for producing different upconverting nanocrystals, such as: hexagonal UCNPs, UCN-dots, DCN-Ds, SAM-SL-UCNPs, are discussed below.

### **2.3.1 Synthesis method for highly efficient hexagonal UCNPs:**

To form hexagonal UCNPs,  $\text{YCl}_3$ ,  $\text{YbCl}_3$ ,  $\text{ErCl}_3$  were mixed in 6 mL of OA and 15 mL of ODE in a 250 mL of three-necked flask on heating mantle, at first the heating started towards  $150^\circ\text{C}$  to create a homogeneous solution and after that started for cooling at room temperature only. 10 mL of methanol solution along with  $\text{NH}_4\text{F}$  and NaOH was prepared and added very slowly (drop wise) into the heating flask. Now to consume all fluoride reagents, the whole sample in flask was stirred for some time. From this condition onwards, slowly it was heated for evaporating methanol from sample-solutions. Thereafter, degassed condition was applied at  $100^\circ\text{C}$  for 10 mins and finally the temperature was fixed at  $300^\circ\text{C}$  for 1 hour which was maintained under complete inert gas atmospheric condition. Cooling was started naturally at room temperature and continued until the sample-flask came to room temperature. Next day, from cooled flask, the nanocrystals were collected with cyclohexane and then washing method using ethanol and water (1:1 v/v) and centrifugation method.

### **2.3.2 Synthesis method for UCN-dots:**

The detailed synthesis procedure of UCN-dots has been filed for Indian patent (Ref. TEMP/E-1/21071/2017CHE, dt.: 14/06/2017). In brief of the synthesis procedure: the specific amount of precursor materials ( $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ ) were dried from moisture and poured in 1-Octadecene and Oleic-acid followed by heating in inert gas environment. Thereafter, at room temperature a mixture (4:1) of NaOH and  $\text{NH}_4\text{F}$  (dissolved in MeOH) was added. The resulted solution was heated in inert gas atmospheric condition up to  $300^\circ\text{C}$  for few mins and then it was cooled down to room temperature. Finally, the UCN-Dots were collected via high speed centrifugation (RPM 14000) and were preserved in cyclohexane.

### 2.3.3 Synthesis method for UCN-Ds:

UCN-Ds were synthesized by solvothermal decomposition process of lanthanide precursors and technical grade chemicals. Three different precursors were prepared in presence of de-ionized H<sub>2</sub>O. These three precursors were then decomposed at 110°C - 115°C. Further, in decomposed compound organic solvents (Oleic acid and Octadecene) were added and stirred at 140° C. Then it was cooled down to room temperature. Then, a solution of CH<sub>3</sub>OH, NH<sub>4</sub>F and NaOH was added at room temperature and stirred to remove excess oxygen and water and heated further to 340° C (rate of 20° C/min). Entire synthesis was performed under argon gas atmosphere and a vacuum condition was maintained at 100° C. Next day, the synthesized sample was collected with acetone via centrifugation with 9000 rpm for 15-20 min. The precipitated product was collected by dispersing with cyclohexane (40ml). Finally, it was washed with ethanol and D.W. (1:1) for 3-4 times. The resulted solution was preserved in a container as its colloidal form. The self-assembled dendritic UCN-Ds are stable for more than a year. Surprisingly, no agglomeration or settling was found. However, after a couple of weeks the white particles seemed to be settled clearly at the bottom of container and it can be readily dispersed at room temperature and subsequent characterization revealed that dendritic net-work structures persist for more than a year. The detail of synthesis method was filed for an Indian Patent (Ref: TEMP/E-1/21065/2017CHE, dated: 14/06/2017).

### 2.3.4 Synthesis method for SAM-SL-UCNPs:

SAM-SL UCNPs were synthesized by using thermal decomposition procedure of lanthanide precursors and technical grade chemicals. The de-ionized H<sub>2</sub>O solutions of hexahydrate precursors were used. Three precursors were decomposed with reaction-temperature of about 120°C. Thereafter, organic solvents (ODE, C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>) were added

and stirred with similar heating rate as in decomposing step. A mixed solution of  $\text{CH}_3\text{OH}$ ,  $\text{NH}_4\text{F}$  and  $\text{NaOH}$  was added at room temperature and stirred vigorously to remove excess oxygen and water and heated further to  $320^\circ\text{C}$  for a maximum of 15-20 minutes, 51 minutes, 1 hour 50 minutes. The experiment was done under complete argon gas atmospheric condition and a vacuum condition was maintained at  $100^\circ\text{C}$  for 30 minutes to produce a yellow and transparent solution. Next day, the synthesized sample was collected via centrifugation with acetone and cyclohexane. Then it was washed with ethanol and D.W. The resulted solution was preserved in container as its turbid, colloidal form.

SAM-SL UCNPs are stable for a couple of weeks and surprisingly, no agglomeration or settling was found during this period, however, after few months particle settling was found.

The detailed synthetic procedure has been filled for an Indian Patent (Stable up-conversion nanoparticle super lattice (UCN-SL) & in-situ process for developing thereof (Ref: TEMP/E-1/21071/2017CHE, dt.: 14/06/2017).

## **2.4 Characterization Techniques Used:**

Different synthesized UCNPs were characterized through several techniques such as , Transmission Electron Microscopy (TEM) , X-ray diffraction pattern( XRD), Raman Spectroscopy, Atomic Force Microscopy (AFM) , Fourier Transform Infrared Spectroscopy (FTIR), Fluorescence Spectrophotometer, Multimode Reader (H4 synergy Reader), Zetasizer( nano- series: Malvern instruments)), Femtosecond-laser luminescence (140 femtosecond, 80 MHz repetition rate). A short description of each technique is given below.

### **2.4.1 Transmission Electron Microscopy (TEM):**

TEM probes the morphologies of an experimental sample. In the present-study, EDXA is attached with TEM instrument (ex. model FEI TecnaiG2-TWIN 200 KV) for providing information about the presence of different elemental compositions. HRTEM (high resolution transmission electron microscopy) images can also be produced with TEM. SAED pattern (selected area electron diffraction pattern) can provide us the structural configurations of a sample. An acceleration voltage of about 200kV -300kV is typically used in TEM to receive higher resolution (0.1 nm) as well as magnification (10000 KX).

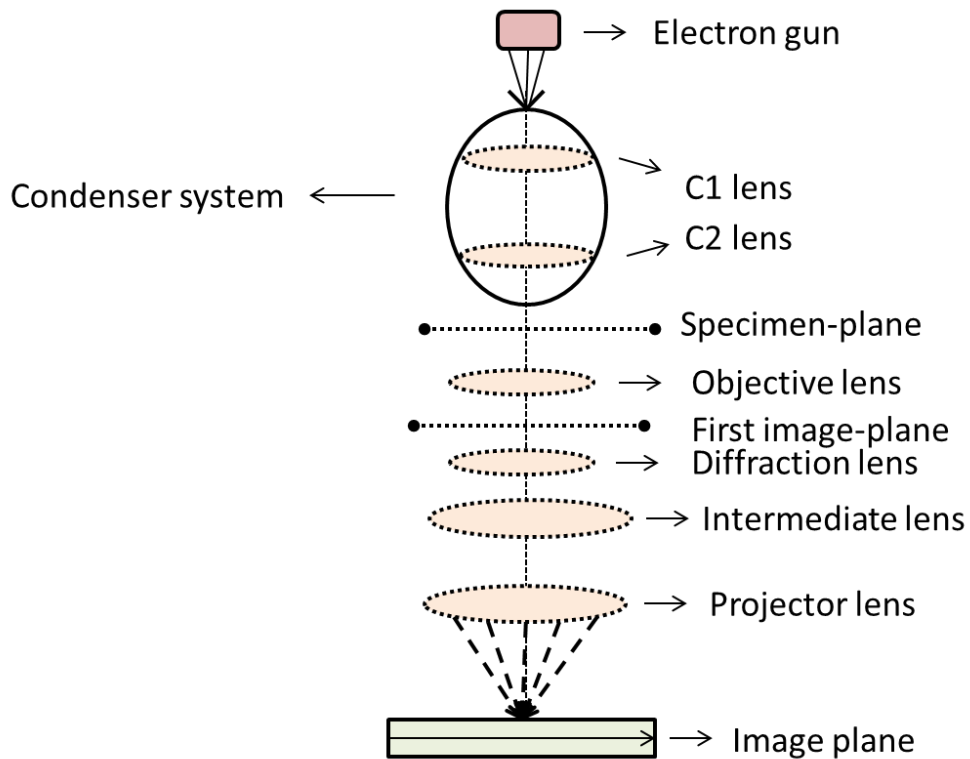
The instrument is carried with three parts,

1. Electron gun with condenser lenses, electron gun generates the electron beam, and condenser lenses focuses accelerated beam.
2. Image-forming system, which basically focus the electrons to generate highly magnified image.
3. Image recording system, which uses objective lenses and a fluorescent screen and a camera to record the focused images.

Besides the presence of them, a vacuum system is also maintained inside the chamber to avoid the ionization of air molecules. Tungsten filament is used to accelerate the electrons. In modern TEM, two condenser lenses are used, say C1 and C2. C1 reduce the spot sizes whereas C2 intensifies the spot. These two lenses control the electron-illuminations on sample. The objective lenses can control the contrast and magnifications of the images formed.

The presence of some mechanisms forms the images on screen, one is Mass-density contrast and the other one is Diffraction contrast.

A diagram of TEM system is drawn in figure 2.3.1,



**Figure 2.4.1: Schematic of TEM system**

**Mass density:** Interaction between electrons and nucleus results in scattering of electrons. Hence, for a sample, the amount of scattering from a specific point of material is dependent on the mass density of that particular specimen-point.

**Diffraction-contrast:** In the formations of images for crystalline materials, diffraction-contrast takes place and undergoes with collective deflection of electrons, which are scattered by crystal planes arranged parallel. Diffraction angle appears to be very small of about  $\leq 1^\circ$ . Diffracted beam from collaboratively scattered electrons are focused as spot. Bright-field image is produced with allowing the transmitted beam while dark field image is produced with only passing diffracted beam.

**Phase-contrast:** Phase-contrast can be introduced as high-resolution transmission electron microscopy (HRTEM) and is different from two amplitude contrasts (Mass density and diffraction contrast). It can produce very high-resolution images of lattices and structures of crystalline specimens. While, amplitude contrasts involve change in amplitude of electron-waves, phase contrast involves two electron-waves in different phases (e.g. transmitted beam and diffracted beam appear in different phases).

However, Special care should be taken to prepare samples for receiving TEM images. Samples are always placed on carbon-coated copper-grid in a complete dried form, which must be having thin-layer, and the electrons get diffracted easily with the specimen-molecules.

For biological samples, special sample preparation techniques are used with applying low acceleration-voltage.

#### 2.4.2 X-Ray Diffraction:

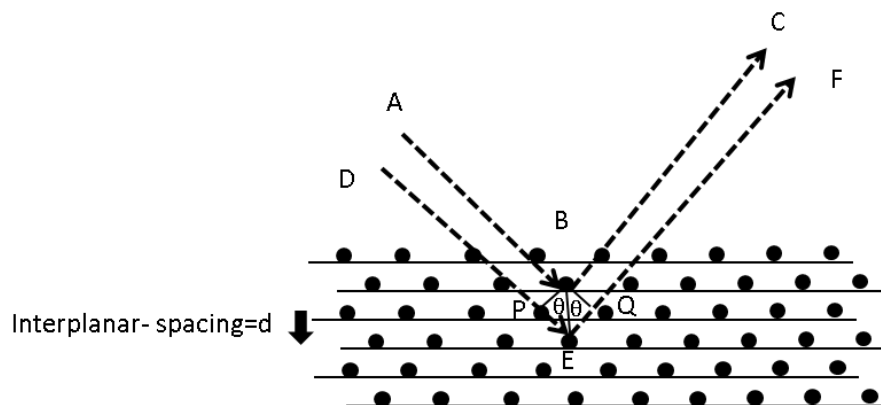
X-ray diffraction is a powerful method to characterize crystalline materials. Crystallinity of sample is strongly determined with this technique. Owing to the presence of different atomic arrays in different materials, the produced diffraction pattern also becomes different. This technique is based on Bragg's law which is defined as  $2d\sin\theta = n\lambda$ , where  $d$ = interplanar spacing between two atomic layers,  $\theta$ = angle at which the beam is diffracted,  $\lambda$ = wavelength of incident light,  $n$ = integer number (reflection order). This law describes, the path difference between two incident x-rays must be equal to  $n\lambda$ . In this dissertation, Bruker AXS model D8 diffractometer has been used with using  $\text{CuK}\alpha$  source to determine crystalline structure of UCN-samples. Again, from this technique, by using Debye Scherrer formula crystallite sizes are calculated which have been reported in result and discussion part. A schematic of XRD technique has been drawn in figure 2.3.2.

According to the figure 2.3.2, path difference between two x-rays =  $PE+EQ$

$PE= d\sin\theta= EQ$

So, total path difference=  $2d\sin\theta$

Now, according to Bragg's law,  $2d\sin\theta = n\lambda$



**Figure 2.4.2: A schematic of XRD technique showing diffraction from two parallel planes**

### 2.4.3 Atomic Force Microscopy:

Atomic Force Microscopy can be considered as one type of high-resolution scanning probe microscopy using a cantilever with short tip (15-30 nm radius) which scans over the materials surface. As this tip approaches towards the sample-surface, it bends due to the presence of attractive force between tip surface and sample-surface. Again, the cantilever bends away from the sample-surface due to an increasing repulsive force between cantilever and sample-surface (while the cantilever comes very closer to material-surface. Additionally, two scanners are present in AFM, one for moving the cantilever up and down and the other one for moving the sample back and forth. To record the bending of cantilever, a position detector is present. Laser beam reflecting on cantilever can be tracked with the position-sensor. Direction of reflected beam can be changed with changing the bend-position of cantilever. The beam-changes are tracked and recorded with position-detector. For any material, the topography of required region appears in AFM image while the cantilever scans over the

specified region. The lowered and raised characteristics of any material-surface are measured with position detector by influencing cantilever-bending. We are able to receive a reliable topographic image of sample-surface by using AFM technique. The schematic of AFM is shown in figure 2.3.3. There are different modes of AFM, they are:

1. Contact-mode AFM: In this mode, the tip touches sample-surface and as a result the cantilever bends while passes over surface-feature. Distance between probe and sample-surface is less than 0.5nm.

Advantage: Relatively simple technology.

Disadvantage: Sample-surface can be damaged sometimes due to the close proximity of sharp-tip and sample-surface.

2. Non-Contact-mode AFM: In this mode, the tip does not touch sample-surface, rather than the cantilever oscillates just over surface-wall. Distance between probe and sample-surface is 0.1- 10nm.

Advantages: This mode permits to give high quality AFM images with prolonged tip-sharpness and tip-lifetime. It can also reduce the operating cost of instrument as no tip-replacement is required for scanning.

Disadvantages: Ultra high vacuum (UHV) is required to receive best images. The oscillation can be disrupted with contaminant layer.

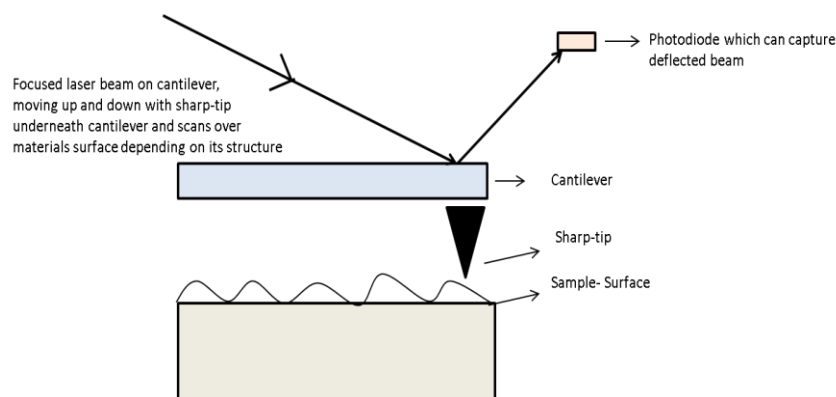
3. Intermittent –contact mode: In this mode, imaging is done specially with soft samples (e.g. biological samples). Using “tapping mode” the deformations (occurs with the exerting force by sharp-tip during scanning) of soft samples can be overcome by this technique which can afford highly sensitive signals by lowering the oscillation-

amplitude of cantilever. Distance between probe and sample-surface is 0.5- 2 nm. Oscillation- amplitude is about 20-100nm.

Advantages: High resolution images are formed and recommended for soft samples

Disadvantages: More challenging in case of liquid-imaging and provides slower scan-speed.

In present study, surface topographical images have been received with non-contact mode in AFM and the model used is Model: SII Oo Seiko Instruments Inc.

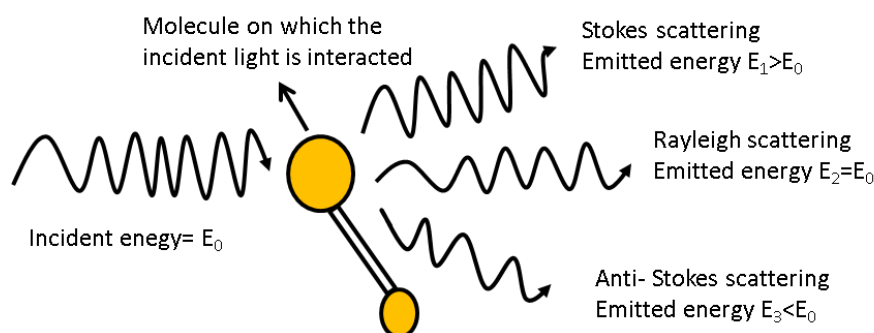


**Figure 2.4.3: Schematic illustrating AFM working principle**

#### **2.4.4 Raman Spectroscopy:**

It is a spectroscopic technique to measure the chemical structure of any substance by detecting the vibrational modes of molecules. This technique is based on the inelastic scattering of photons which comes from monochromatic light source. The study of interaction between light and matter is observed in this technique and is termed as Raman Effect. During interaction of light with matter, the photons undergo different effects as they can be scattered or transmitted or reflected or can be absorbed fully or partially. In scattering effect, elastic (Rayleigh scattering) or in-elastic (stokes and antistokes scattering effect) scattering can take place. In Raman spectroscopy, we deal with in-elastic scattering of photons with stokes or

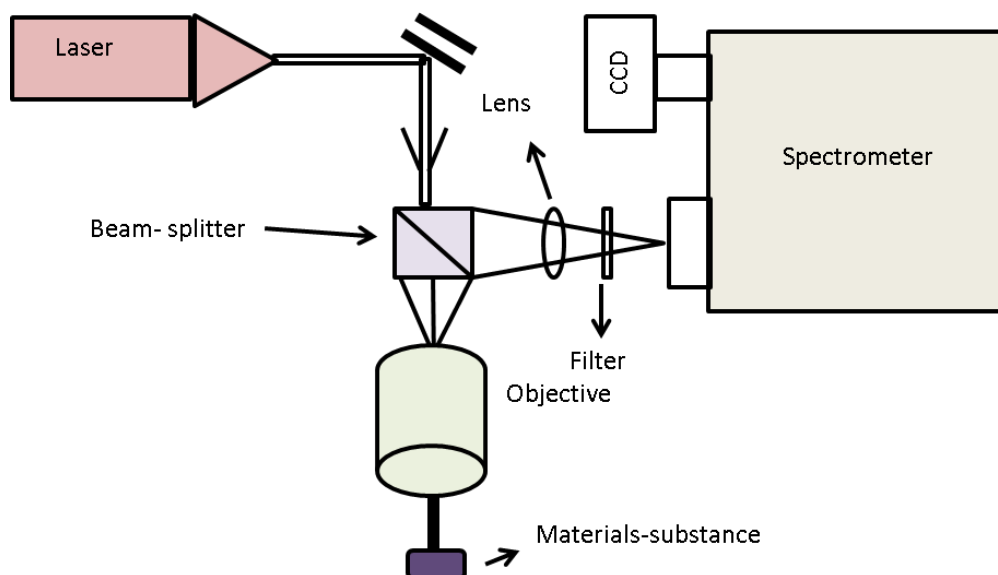
antistokes shifts. These shifts can provide us the information of different modes in interacted molecules (vibrational mode, rotational mode or other transition modes). This spectroscopy is used for solid, liquid and gaseous substances. Distinguishing different modes in Raman spectra, one can confirm the presence of molecules and the associated functional-groups in any specified substance.



**Figure 2.4.4: Schematic of Raman scattering effect after interacting with substance-molecule**

The Raman spectra that we receive from Raman spectroscopy provide us various information on substance-molecules. We can interpret them in terms of either wavelength or energy. The spectra received in higher wavelength region compared to Rayleigh scattering line, originate due to antistokes scattering phenomena and the spectra received in lower wavelength region, occur due to stokes scattering effect (figure 2.3.4). So, the stokes lines always appear with higher intensity.

In Raman instrumentation, laser light is projected on sample by using single-wavelength laser source. The instrument integrates with optical microscope. Using micro Raman spectroscopy technique, we can analyze micro areas in large substance. The modern micro Raman instruments use several single-wavelength sources to avoid resonance effect. In order to produce, good Raman signals, excitation sources can be varied with varying excitation wavelengths. A schematic of Raman-instrumentation is shown in figure 2.3.5.



**Figure 2.4.5: Schematic representation of Raman spectroscopy instrumentation**

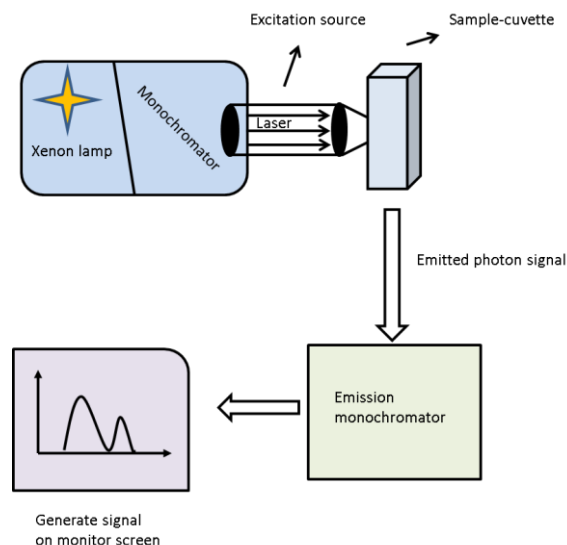
In this dissertation, samples have been characterized using “Witech Alpha 200 Raman spectrophotometer” model containing Nd YAG laser (532nm excitation Wavelength) with 2<sup>nd</sup> harmonics and spot size of about 2  $\mu\text{m}$ .

## 2.4.5 Fluorescence Spectroscopy:

Fluorescence from any sample-molecules is being studied with fluorescence spectroscopy technique. It has become a powerful technique to study the chemical or physical properties of molecules due to high sensitivity. In this technique, near infrared or infrared light source is generally used to impinge on sample-molecules and the resulted fluorescence spectrum is recorded. This measurement can provide emission spectra as well as excitation spectra (due to presence of dual modes). In case of receiving emission spectra, we need to fix excitation-wavelength with varying the detector scanning- wavelength and in case of receiving excitation spectra, we need to fix detector scanning- wavelength with varying excitation-

wavelength. The mechanism behind this technique is based on the presence of different energy levels with their vibrational states in molecules. While the light source impinges on the sample-molecules, the molecules become excited and jump to excited state from their ground state vibration levels. Due to efficient populations in higher excited-states or due to collision with other molecules, the excited molecule immediately comes to lowest vibrational level from which they can reach to ground state. Here, the extra energy comes out in terms of emission and is recorded in fluorescence spectroscopy with fluorescence spectra. Fluorescence intensity can be varied with different efficient populations present in different excited energy-states depending on different molecular configurations of chemical compounds.

In this dissertation work, Hitachi F-4600 spectrophotometer model is used and as excitation source Xenon lamp is present in instrument. Furthermore, an external source of 980nm excitation wavelength NIR-laser is attached with this spectroscopy. A basis diagram of Fluorescence spectroscopy is shown in figure 2.3.6.



**Figure 2.4.6: A simple schematic of fluorescence spectroscopy instrumentation**

#### 2.4.6 Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is a spectroscopic technique to receive infrared spectrum of emission, absorption or Raman scattering of any substance (solid/liquid/gas). This spectrometer accumulates high-resolution spectral data over wide range. By this technique, the actual data are being transformed with Fourier transform (known as a mathematical algorithm and Lord Rayleigh introduced the existence of relation between spectrum and interferogram via Fourier transform). The sample -molecules absorb certain frequencies which provide the particular characteristics of chemical – structures. Hence, the resonant frequencies occur as the absorbed radiation matches with the bond/group- frequency under vibration.

Instead of single wavelength source (ex. Monochromatic light), FTIR uses beam carrying many frequencies. Such beam with many frequencies is being modified to provide second data point and this process repeat several times and finally computer records all datas for absorptions at each wavelength. Michelson interferometer (MI) is the core part of FTIR as MI recombines two beams to conduct them into detector.

Sample preparation can be done with few steps:

Step 1. For using solid sample in FTIR, 200mg KBr is required with 2 mg of sample. For liquid samples, NaCl pellets are generally taken, for volatile liquid sample, sample-solution is prepared with CS<sub>2</sub>/CCl<sub>4</sub>.

Step 2. In this step we get spectrum by collecting interferogram thereafter these raw data is being converted to frequency data via inverse Fourier transform process.

Step 3. In this step we collect the absorption bands (and also the background spectrum) of sample from recorded spectrum.

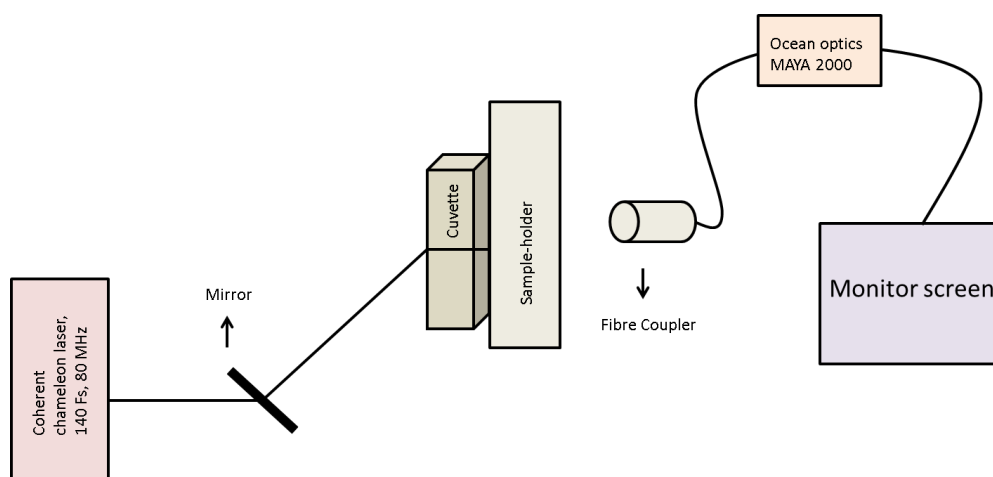
Step 4. The ratio of the sample-spectrum and background spectrum of single beam can provide the required spectrum for analysis.

Step 5. Now, we can analyze data by observing absorption frequency bands in spectrum and by assigning them to proper vibrational modes of molecules.

In this work, an FTIR spectroscopy- Nicolet model impact-410 has been used.

#### 2.4.7 Femtosecond laser (Fs) set-up:

At present days, upconversion luminescence based on  $2/2$  photons (absorbing simultaneously) has drawn our attention due to an advanced technology in NIR Fs laser which can develop highly sensitive organic materials. Compared to the other lasers, NIR Fs - Laser give several merits as they can penetrate deeper in tissues/bulk materials.



**Figure 2.4.7: An schematic diagram of Femtosecond laser-set up with 140 Fs, 80MHz repetition rate**

In present work, A Ti-Sapphire tunable oscillator laser with pulse duration of 140 femtosecond at a repetition rate of 80MHz (coherent chamemeon ultra-II) has been used as pumping source for sample excitation. Signal is recorded with non-gated spectrometer (Ocean optics, MAYA 2000). A schematic representation of this set-up is shown in figure 2.3.7.

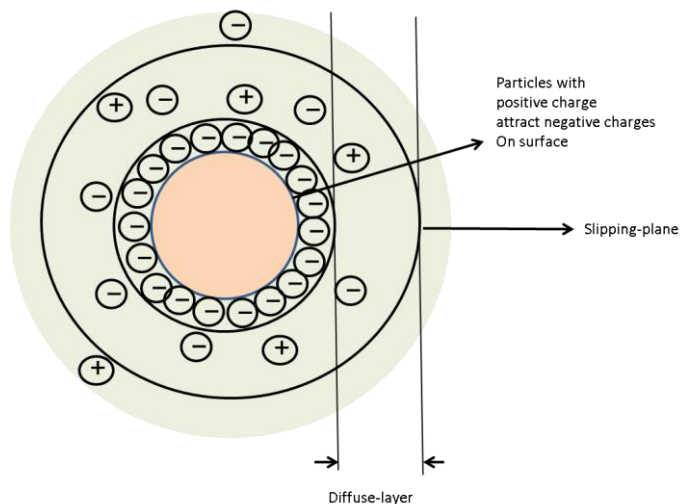
#### **2.4.8 Photoluminescence with Multimode Reader:**

Multimode reader device can detect reactions in samples with emitted light and can quantify them. In this technique, we can operate different detection-modes to perform and measure different experiments simultaneously such as: luminescence, fluorescence and absorbance (the most widely used modes). Besides them some advanced-modes are also available in present devices. Multiwell plates are used in this instrument for holding samples. Different samples can be performed at once by placing 1-2 drops of sample in well-plates. Generally, photomultiplier tubes (PMT tubes) are used for detecting light signal. The sensitive detector can convert the incoming photons into electricity which can be further quantified by this reader. Exciting the samples by light at certain detection modes and wavelengths we can receive output which appears with numbers quantifying the intensity of emitted light interacted by sample in plates. Hence, xenon lamp is used as excitation light source and to produce a certain excitation wavelength a specific excitation filter is used with lamp source. Though, generally such filters are employed between sample and detector but sometimes, to enhance the sensitivity and specificity, filters are placed in detection-side. For determining the experimental values, a standard curve is utilized for experiments on plate reader. For generating best fit line of standard curve sample of known concentration is used, thereafter, using linear regression experimental values can be extrapolated.

In this dissertation, Synergy H4 Hybrid Reader has been used in photoluminescence mode with fixing excitation wavelength at 450nm.

#### 2.4.9 Zetasizer nano series:

This instrument can measure three different parameters of particles suspending in liquid medium and they are: particle sizes, molecular weight and zeta potential over wide range of sample-concentrations. However, present dissertation studies only zeta potential measurements with this instrument.



**Figure 2.4.8: A diagram to understand the phenomena for arising zeta potentials while electric field is applied on sample.**

Ions containing in liquids exist with positive or negative charged atoms- so called anions and cations, respectively. On the surfaces of suspending charged particles the charged atoms( oppositely charge atoms) get attracted i.e. negative charged ions get attracted on positive charged particle- surface and positive charged ions get attracted on negative charged particle- surface by electrophoresis method( A method by which electric field is applied through electrolytes). In this way, the ions bound strongly on suspending particle-surface. So, the diffuse layer with weakly bound ions appears further away of particle. Inside the boundary of diffuse layer ions can move with the suspending particles in liquid- this boundary of diffuse layer is termed as slipping-plane. The potential existing at slipping plane - is known as zeta

potential. The zeta potential value (magnitude of potential value) is a measurement of potential stability of experimental- sample. The large value of zeta potential ( $\xi$ ) is indicative of stable particles owing to existence of repelling factor between similar charged particles and because of that flocculation tendency (a tendency that particles come together) becomes very less or zero. Generally,  $\xi$ - value appearing with more positive or more negative than +30mV or -30 mV, respectively, is considered as stable colloidal system.

In this research work, Malvern Instrument; Zetasizer nano series has been used to record zeta potential values and in sample holder gold-plated brass (copper/zinc/beryllium) has been used as electrolytes. A diagram, explaining the theory that how the zeta potential appears in charged sample, is shown in figure 2.3.8.

### **3 RESULT AND DISCUSSION**

#### **PART I**

##### **3.1 (Part-I): Synthesis of pure hexagonal UCNPs with highly efficient upconversion fluorescence/luminescence:**

###### **Outcome:**

**Monami Das Modak**, Damarala Ganesh, Anil Kumar Chaudhary, Pradip Paik, Structural and spectroscopic Properties of up converting nanoparticles: Thin-Film spectra under Femtosecond laser source, Conference proceedings, Fourth International Conference on Nanotechnology for better living (NBL).

### **3.1.1 Introduction:**

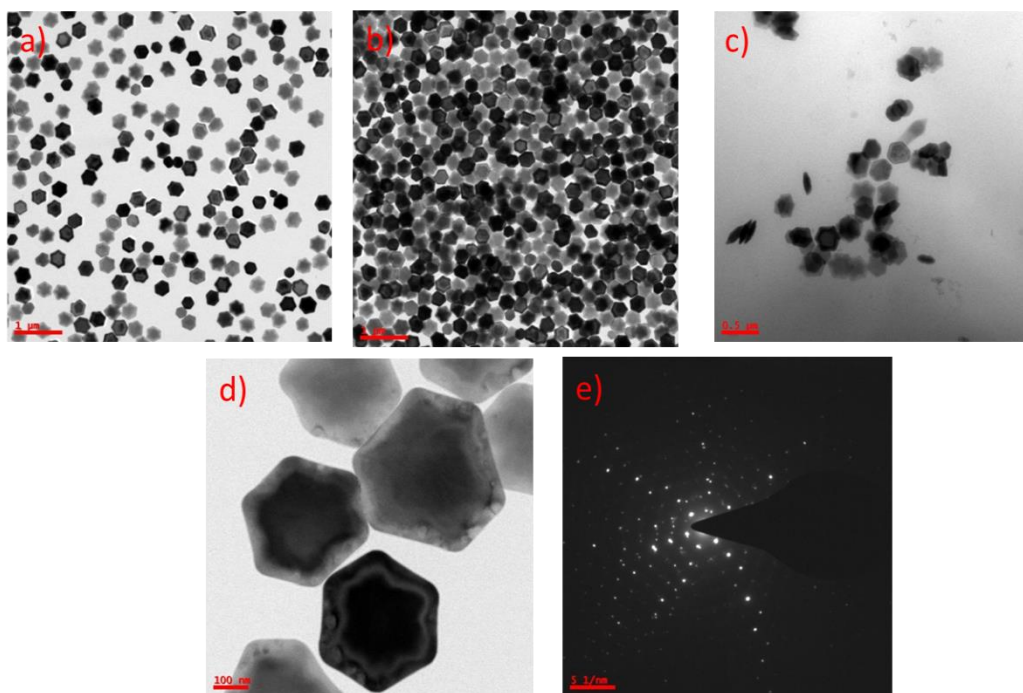
UCNPs have potential applications in display technologies, biolabels, and bio-imaging agents. Recently, UCNPs have attracted our attention as they are able to convert light of longer wavelengths into shorter one through photon-upconversion process. Their superior spectroscopic properties make them unique while dealing in biomedical applications, especially in bio-medicine therapeutic agents. Synthesis of UCNPs is a challenging task. Till date, hexagonal phases of UCNPs (e.g.,  $\text{NaYF}_4\text{:Yb}^{3+}; \text{Er}^{3+}$ ) have proven to be the most efficient upconverters due to highly intense visible emission under UV/NIR excitation source. In this context, I have synthesized highly intense UCNPs in in-situ conditions and their upconversion behavior for the first-time using Femtosecond-laser under 980nm excitation source.

### **3.1.2 Objectives:**

1. Preparing high quality, uniform monodisperse nanocrystals with strong upconversion fluorescence.
2. Avoiding mixed crystalline phases and formation of non-uniformity.
3. To form  $\text{NaYF}_4$  nanocrystals at lower reaction temperature and thereafter increasing high temperature ( $> 300^\circ\text{C}$ ) to improve the quality and uniformity.

### **3.1.3 Morphological studies of $\beta\text{-NaYF}_4$ nanocrystals:**

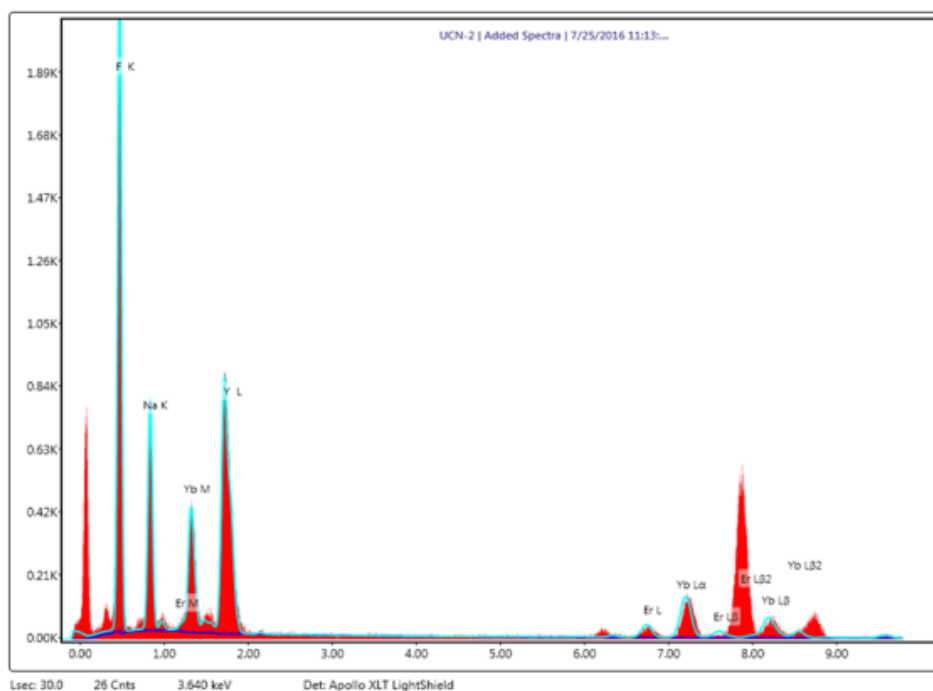
The morphological studies reveal the formations of hexagonal UCNPs which contain uniformity throughout the sample. Figures 3.1.1(a,b,d) shows the hexagonal formations whereas figure 3.1.1c represents their plate-like formations. The SAED pattern shown in 3.1.1e confirms high crystallinity of synthesized materials.



**Figure 3.1.1:** TEM images of of the synthesized hexagonal UCNPs, clear hexagonal formations with scale bar  $1\mu\text{m}$  (panel-a,b);  $500\text{nm}$  (panel-c);  $100\text{nm}$  (panel-d); SAED pattern (panel-e).

#### 3.1.4 EDAX analysis:

The corresponding EDAX spectrum is shown in figure 3.1.2 confirming the presence of elemental compositions. A table is drawn showing the elements present in synthesized compound in table 3.1.1.



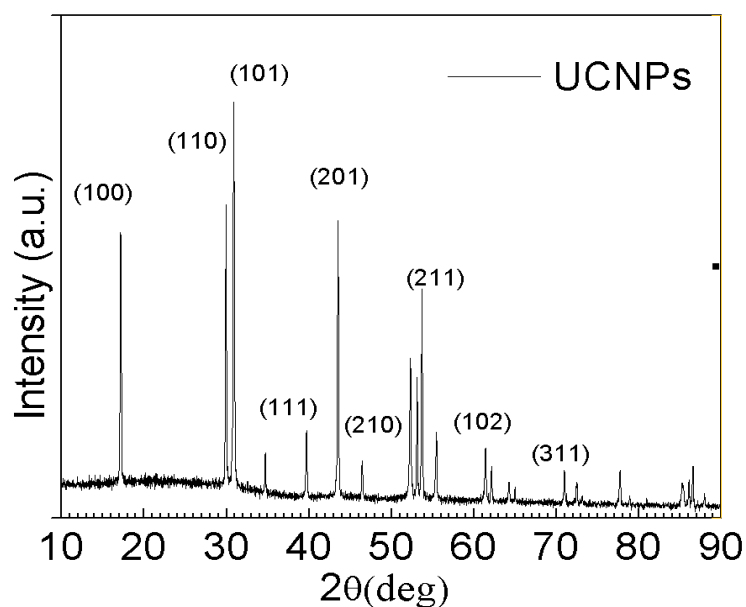
**Figure 3.1.2** TEM-EDAX spectrum of synthesized  $\beta$ -NaYF<sub>4</sub> nanocrystals showing the presence of elemental compositions.

**Table 3.1.1: Elemental compositions in synthesized  $\beta$ -UCNPs**

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| O       | 4.05       | 5.19       |
| F       | 51.45      | 55.59      |
| Na      | 43.79      | 39.11      |
| Er      | 0.13       | 0.02       |
| Yb      | 0.35       | 0.04       |
| Y       | 0.23       | 0.05       |

### 3.1.5 X-ray diffraction analysis:

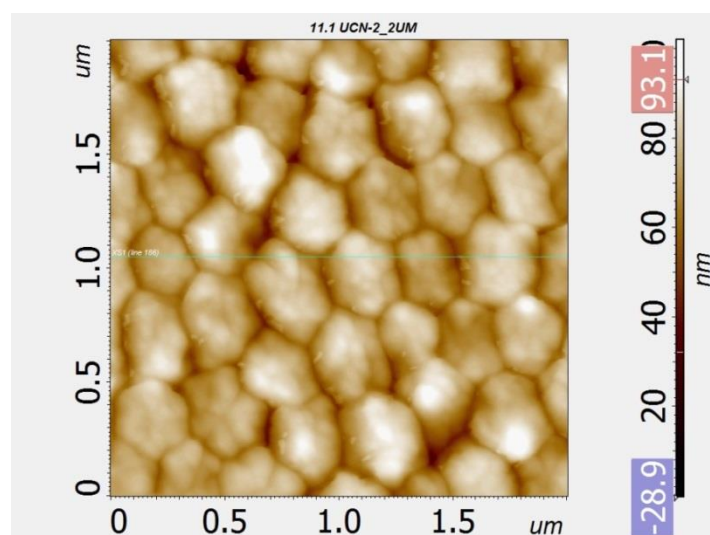
The presence of crystalline planes has been confirmed by x-ray diffraction study shown in figure 3.1.3, the crystalline planes appeared indicate the appearances of crystalline hexagonal phases in solid-state structures. There are no diffraction peaks assigning any cubic phases or impurities indicating a successful synthesis of pure hexagonal UCNPs. According to the JCPDS: 28-1192 pattern the crystalline planes have been found to be (100), (110), (111), (201), (210), (211), (102), (311) appearing with well-defined XRD peaks.



**Figure 3.1.3: XRD pattern of the resulted  $\beta$ -UCNPs confirming the presence of different crystalline planes**

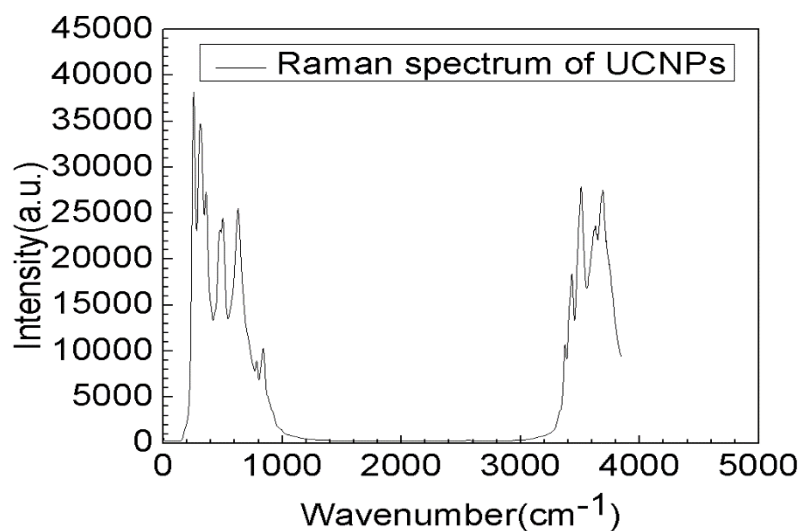
### 3.1.6 AFM study:

The AFM study is shown in figure 3.1.4 confirming the appearance of perfect hexagonal nano crystals. This result is matching well with TEM, XRD and Raman analysis.



**Figure 3.1.4:** AFM study reveals the formation of perfect hexagonal shapes in  $\beta$ -NaYF<sub>4</sub>

### 3.1.7 Raman spectroscopic analysis:

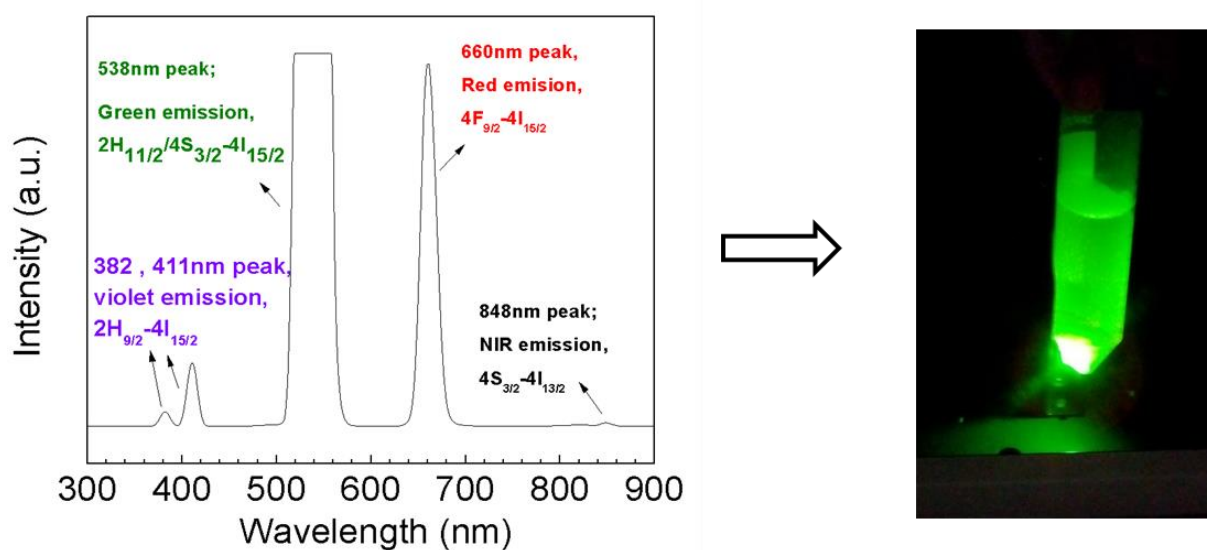


**Figure 3.1.5:** Raman study of  $\beta$ -NaYF<sub>4</sub> confirming the appearances of strong hexagonal phases below 1000cm<sup>-1</sup>

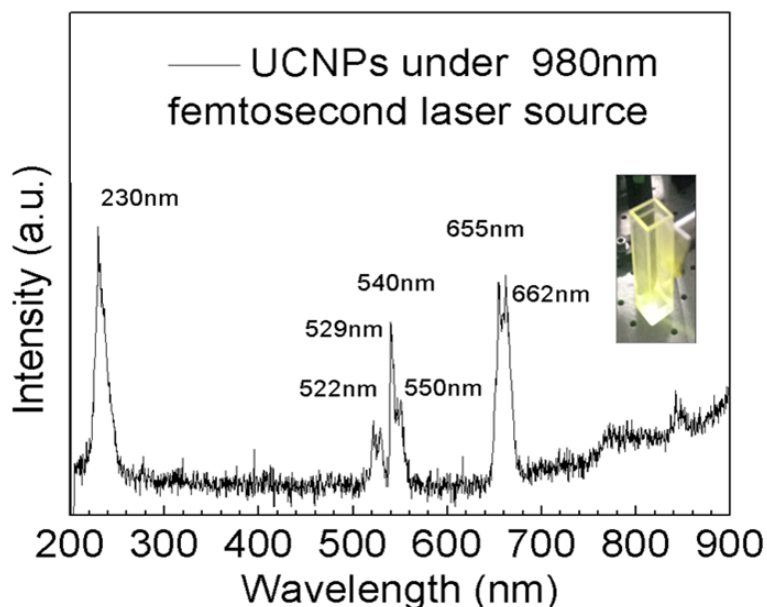
The Raman spectrum shown in figure 3.1.5 shows clearly the appearances of hexagonal phases as most of the strong vibrational modes are appeared below  $1000\text{cm}^{-1}$ . Higher frequency modes above  $3000\text{ cm}^{-1}$  confirm the presence of organic solvents (Oleic acid as major capping agent) in synthesized nanoparticles and formation of pure  $\beta\text{-NaYF}_4$

### 3.1.8 Upconversion fluorescence study:

The upconversion fluorescence study for  $\beta\text{-NaYF}_4$  is shown in figure 3.1.6, where violet emissions corresponding to  $2\text{H}_{9/2} - 4\text{I}_{15/2}$  transition appears at 382nm and 411nm. Green emission corresponding to  $2\text{H}_{11/2} / 4\text{S}_{3/2} - 4\text{I}_{15/2}$  transition appears at 538nm, red emission corresponding to  $4\text{F}_{9/2} - 4\text{I}_{15/2}$  transition appears at 660nm and NIR emission corresponding to  $4\text{S}_{3/2} - 4\text{I}_{13/2}$  appears at 848nm. The photograph of visible green emissions for 1 wt% colloidal solution in figure 3.1.6 indicates the strong emissions under 980nm NIR.



**Figure 3.1.6: The upconversion fluorescence spectrum shows violet, green and red emissions under the excitation of 980nm laser-diode**



**Figure 3.1.7: The intense emissions both in UV and in visible range upon interaction with femtosecond laser 980nm excitation source. The intense shows the visible emissions**

Figure 3.1.7 represents the spectra after interaction of synthesized hexagonal UCNPs with femtosecond laser source maintaining 980nm excitation wavelength. Thus, emissions appeared at 230nm, 522nm, 529nm, 540nm, 550nm, 655nm, 662nm under 980nm excitations confirming their appearances in UV (230nm) and visible (520nm-670nm) region. The inset inside figure 3.1.7 shows visible green emissions under 980nm excitations.

### 3.1.9 Summary of Part-I:

To the best of this author's knowledge, the as-synthesized NaYF<sub>4</sub> nanocrystals with Yb<sup>3+</sup> and Er<sup>3+</sup> are the best UCNPs reported so far as they yield fluorescence even after decreasing the laser power density below 50 mW/cm<sup>2</sup>. During synthesis, all the fluoride reactants were

consumed into solid-state NaYF<sub>4</sub> nuclei at lower reaction temperature (~60°C) as in higher reaction temperature consuming all fluorides become very unfriendly and unsafe to users.

The smaller surfaces of larger sized nanoparticles possess fewer amounts of surface defects, which could be the reason of strong fluorescence.

However, synthesis of such plate-like hexagonal UCNPs has substantial perspective in imaging, solar cells and different display devices and technologies.

## **Chapter 3 RESULT AND DISCUSSION**

# **PART II**

### **3.2 (Part-II): Upconverting nanodots and generation of high energy upconversion through Ti: sapphire 140-femtosecond laser pulses**

**Outcome:** Monami Das Modak, Ganesh Damarla, Anil K Chaudhury, K Santhosh Kumar, Somedutta Maity, and Pradip Paik ; Upconverting nanodots and generation of high energy upconversion through Ti: sapphire 140-femtosecond laser pulses; Manuscript is assigned in arxiv with as permanent identifier 2008.06783 .

### 3.2.1 Introduction

Upconversion phenomenon is a two photon-(one from sensitizer ion and other one from activator ion) process followed by energy transfer (ET) which contributes higher photon energy in ultraviolet (UV) and visible region under the excitation with Infrared (IR) or near infrared (NIR) radiation. The transmutation of IR/NIR photons to UV/visible photons in upconversion nanoparticles (UCNPs) make them unique for applications in electronics and biomedicines. Though there are a few lanthanide ions manifesting upconversion but substantially  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  trivalent lanthanide ions have been used to synthesize upconversion nanocrystals due to their efficient upconversion emission[16], [88], [254].

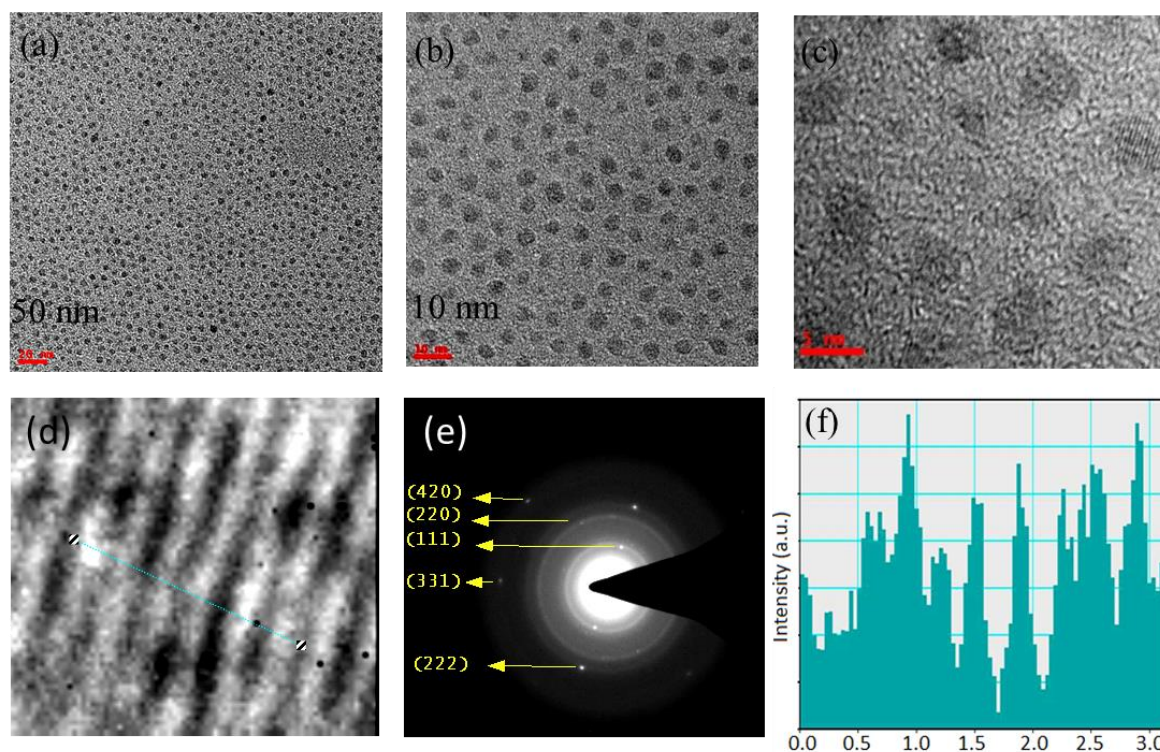
Till date,  $\text{NaYF}_4: \text{Yb}^{+3}, \text{Er}^{+3}(\text{Tm}^{+3})$  has been proven to be one of the most efficient UCNPs[3], [16], [89] due to its highest photon upconversion efficiency. It is well known that smallest luminescent-particles have been always demanding and they attract nano medicines for therapeutic applications [6,7] including bio-labelling [257], in-vivo imaging [258], bio-conjugation,[259] long term cell tracing [260] and bio-detection [261]. Owing to strong biological relevance UCNPs are useful for both in vitro and in vivo applications along with molecular bio-imaging and for targeted cancer therapy [33], [111], [262], [263]. Therefore, it would be a superior idea to combine both of the approaches. It is also reported that UCNPs can be used for solar cells, photovoltaic and plasmonic devices and also for increasing efficiency of several display devices[6], [264]–[268].

Here in this work UCN-dots have been prepared through one-pot chemical-synthesis approach. These UCN-dots are having diameter below 4 nm. All the other works reported so far contained sizes above 10 nm (dia.) and mostly appeared with hexagonal crystalline phases[1–3,5,23]. However, UCN-dots reported in this work have been synthesized within a very short period of reaction time. Short reaction period at moderately high temperature avoids the production of large NaF crystal-matrix and it could also avoid the production of

other fluorinated oxygen and carbon species during synthesis. The second objective of this part of work is to study the upconversion properties of UCN-dots with femtosecond laser source (Ti-sapphire femtosecond laser of 140-femtoseconds duration at 80 MHz repetition rate).

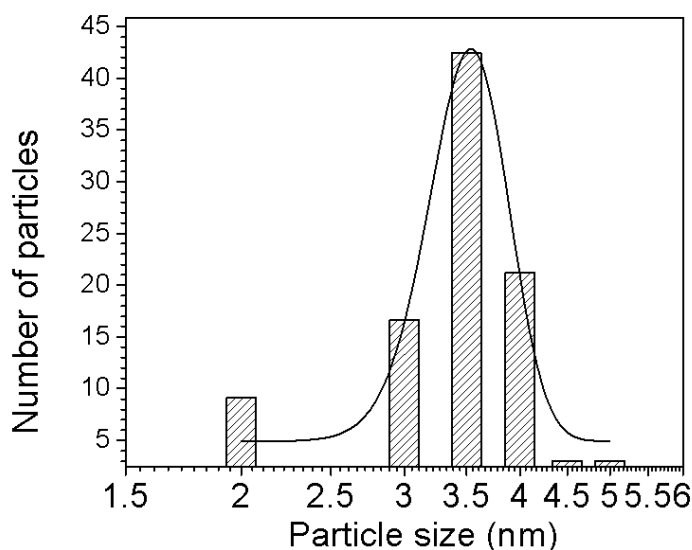
### 3.2.2 Materials Characterization:

UCN-dots were synthesized as discussed in the experimental section and characterized through the several suitable methods.



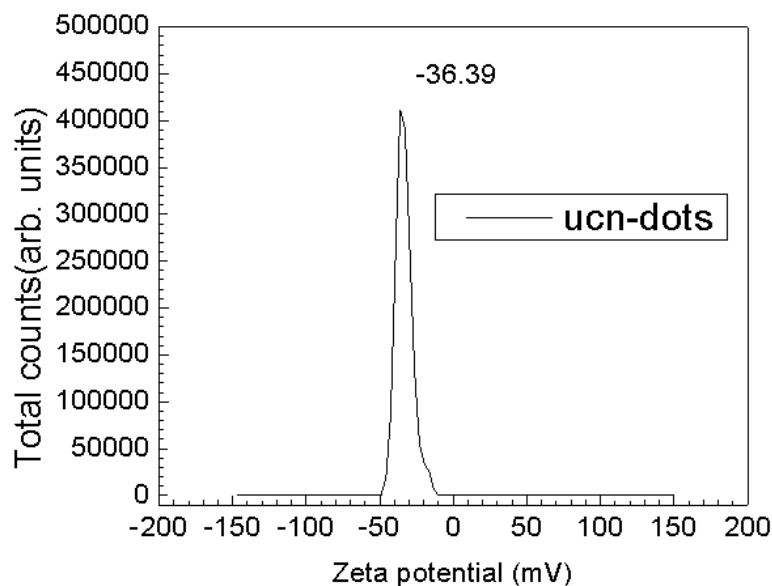
**Figure 3.2.1: (a), (b) and (c) TEM micrograph of UCN-dot: low to high magnification. (c) Represents the fringes of the particles (d) Magnified image of the fringes. (e) Represents the selected area electron diffraction pattern (SAED) obtained from TEM and (f) profile of the fringes**

Figures 3.2.1(a-c) show the TEM micrographs of the synthesized UCN-dots ( $\text{NaYF}_4:\text{Yb}^{3+}; \text{Er}^{3+}$ ) which possess uniform particle size distribution confining size below 4 nm in diameter and they are monodispersed in nature. These UCN-dots are appeared with average size  $\sim 3.4 \pm 0.15$  nm in diameter (figure 3.2.2) and stable up to one year due to their high surface zeta potential of -36.39 mV (figure 3.2.3).



**Figure 3.2.2: Histogram particle size and distribution calculated from TEM micrograph**

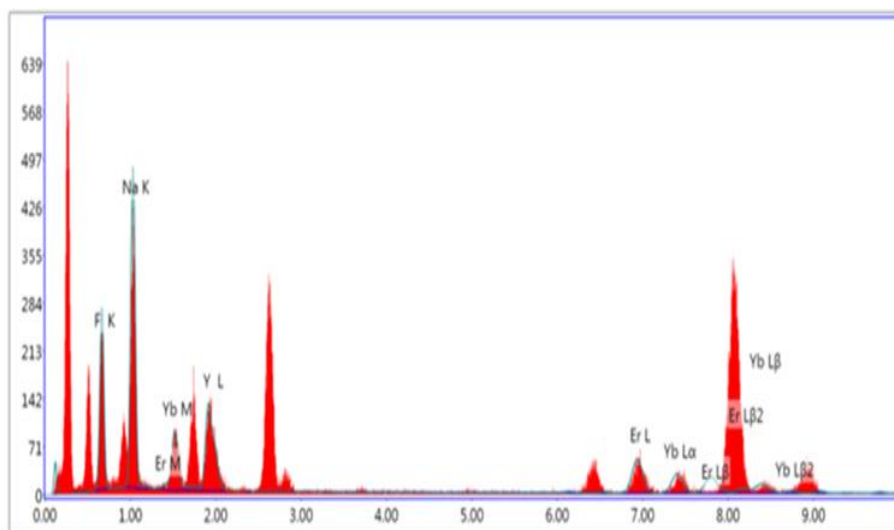
Figures 3.2.1(c,d) shows high resolution TEM , HRTEM micrographs with clearly exhibiting the lattice fringes which confirms the crystallinity of synthesized dots. Distance between two adjacent fringes has been calculated to be 3.1 Å. Figure 3.2.1e shows SAED pattern (ring pattern) corresponding to the (111), (220), (222), (331) and (420) reflection planes for pure cubic crystal structure which further have been confirmed through the XRD and Raman spectroscopy and explained in the subsequent sections.



**Figure 3.2.3: Zeta potential for colloidal UCN-dot sample**

Crystal structure of solid powder UCN-dots has been confirmed through XRD shown in figure 3.2.5 which confirms the well-defined diffraction peaks at  $2\theta = 31.8^\circ$ ,  $45.5^\circ$  and  $66.3^\circ$  corresponding to the reflection planes (111), (220) and (222) respectively and represents the appearance of cubic (FCC) crystalline phases in UCN-dots. Crystallite size has been calculated using Debye-Scherrer formula[2,24] and the average crystallite size has been found to be  $\sim 3.4 \pm 0.15$  nm. The Lattice parameters for cubic crystalline UCN-dots have been evaluated to be  $a = 5.51$  Å,  $b = 5.31$  Å and  $c = 5.32$  Å which is matching well for the cubic phases of UCN nanoparticles reported[127]. The elemental composition is confirmed with EDAX analysis (figure 3.2.4 and table 3.2.1). From XRD (figure 3.2.5) and from the EDAX (figure 3.2.4) results the number of unit cells present in a single UCN-dot has also been calculated and found to be: 143 [calculation part is shown at the end of this part II]. It can be noted that the number of different atoms present in a unit cell of UCN-dots are 2, 8, 1 and 1 for

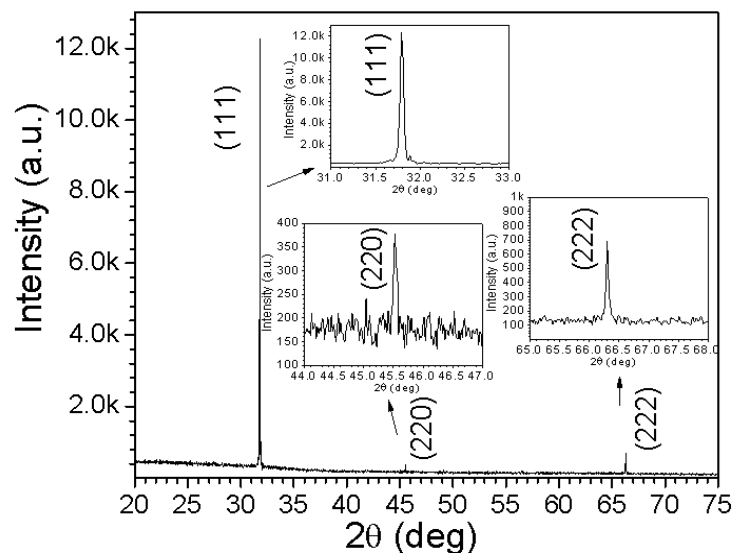
Na, F, Yb and Er, respectively as a fraction of  $Y^{3+}$  ions are substituted by rare earth ions ( $Yb^{3+}$  and  $Er^{3+}$ )[270].



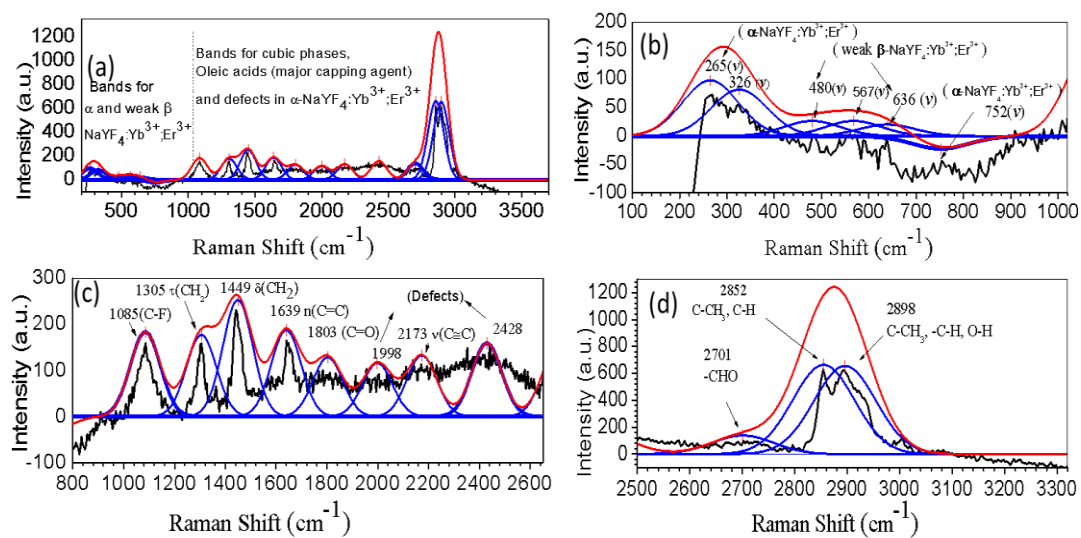
**Figure 3.2.4** EDAX analysis of UCN-dots colloidal sample

**Table 3.2.1:** Table for elemental analysis from EDAX

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| F       | 25.23      | 29.33      |
| Na      | 73.34      | 70.47      |
| Er      | 0.85       | 0.11       |
| Yb      | 0.43       | 0.05       |
| Y       | 0.16       | 0.04       |



**Figure 3.2.5: XRD of UCN-dots represents the crystalline phase (cubic, FCC) of UCN-dot. In sets are showing enlarge peaks for (111), (220) and (222) planes**



**Figure 3.2.6: Raman Spectra for the UCN-dots, (a) for the full region. (b) band region 100 cm<sup>-1</sup> to 1000 cm<sup>-1</sup> representing the major  $\alpha$ -phase of  $\text{NaYF}_4\text{:Yb}^{3+}\text{:Er}^{3+}$  dots, (c) 800 cm<sup>-1</sup> to 2600 cm<sup>-1</sup> and (d) 2500 cm<sup>-1</sup> to 3300 cm<sup>-1</sup>, exhibiting the presence of major capping agents in cubic phases**

Figure 3.2.6 shows the Raman spectra of the UCN-dots appeared in different band regions. Figure 3.2.6a shows the entire spectra where most of the bands appeared between 100-1000  $\text{cm}^{-1}$  represents the appearance of cubic phases in UCN-dots ( $\alpha\text{-NaYF}_4\text{:Yb}^{3+};\text{Er}^{3+}$ ) whereas, band region appeared between 1000  $\text{cm}^{-1}$  -3500  $\text{cm}^{-1}$  confirms the presence oleic acids (capping agent). Weak Raman bands with phonon frequency below 1000  $\text{cm}^{-1}$  confirm the presence of vibrational modes ( $\nu$ ) of  $\alpha\text{-NaYF}_4$  or  $\beta\text{-NaYF}_4$  crystals.

Hence, below 1000  $\text{cm}^{-1}$  phonon vibrational bands (with its maximum position) appeared at 265  $\text{cm}^{-1}$ , 326  $\text{cm}^{-1}$ , 480  $\text{cm}^{-1}$ , 567  $\text{cm}^{-1}$ , 636  $\text{cm}^{-1}$  and 752  $\text{cm}^{-1}$  (figure 3.2.6b) further satisfy the presence of major  $\alpha$ -phases along with relatively less extent of  $\beta$ -phases in UCN-dots [271]–[273].

However, presence of weak  $\beta$ -phases is identified with band positions at 480  $\text{cm}^{-1}$  and 636  $\text{cm}^{-1}$ . Other bands appeared at 326  $\text{cm}^{-1}$  and 567  $\text{cm}^{-1}$  can be ascribed for distinct vibrations originated from newly synthesized UCN-dots with  $\alpha$ -phases. The high frequency phonon energy modes appeared at 1085  $\text{cm}^{-1}$  and 1305  $\text{cm}^{-1}$  correspond to the presence of C-F and -CH<sub>2</sub> groups respectively.

The bands are appeared at 1449  $\text{cm}^{-1}$ , 1639  $\text{cm}^{-1}$ , 1803  $\text{cm}^{-1}$ , 2173  $\text{cm}^{-1}$  and 2701  $\text{cm}^{-1}$  due to the presence of CH<sub>2</sub>, -CH<sub>3</sub> groups, -C=C- bond, -C=O bond, -C $\equiv$ C- and -CHO, respectively of oleic acid (capping agent) (figures 3.2.6c and 3.2.6d). Two weak intense bands appeared at 1998  $\text{cm}^{-1}$  and 2428  $\text{cm}^{-1}$  due to the possible defects present in UCN-dots (figure 3.2.6c).

However, bands for  $\beta\text{-NaYF}_4\text{:Yb}^{3+};\text{Er}^{3+}$  are found very weak and only bands for prominent  $\alpha\text{-NaYF}_4\text{:Yb}^{3+};\text{Er}^{3+}$  are present in UCN-dots. Further, the weak bands appeared in between 687-703  $\text{cm}^{-1}$  and 260-279  $\text{cm}^{-1}$  along with the broad band in between 750-1750  $\text{cm}^{-1}$  are confirmed for fcc -  $\alpha\text{-NaYF}_4\text{:Yb}^{3+};\text{Er}^{3+}$ . Thus, for Raman it is confirmed that UCN-dots prepared in this work is with cubic crystalline phases which can be complied with the results obtained from figures 3.2.1e and 3.2.2. The possible reasons for appearance of the higher

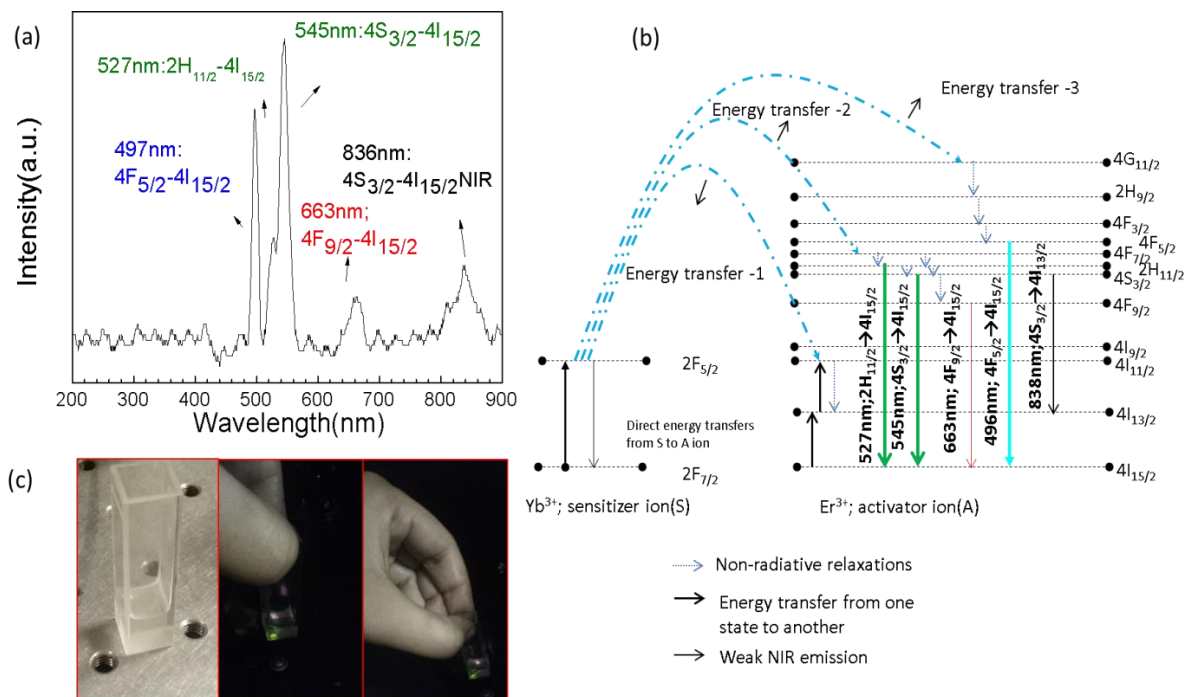
frequency bands in raman spectra are: (i) the dimensions of particles are very small due to which a higher number of capping agents are being absorbed on the surface, as a result high energy C-H or C-C vibrations can be caused of getting higher frequency raman bands, (ii) presence of functional groups ( $\text{O}=\text{C}-\text{O}^-$  and  $\text{OH}^-$ ) in oleic acid attached on the surface of the particles and (iii) finally, a higher percentage of capping agents and their functional groups on UCN-dots can act as surface active agents which can initiate a compressive stress leading to closely packed surface atoms and as a result of vibrations, raman peaks are appeared with extended band positions.

### 3.2.3 Upconversion fluorescence with CW-980 nm laser source:

Up-converted materials qualify the inclusion of two or more photons resulting in the emission of higher energy photons through several energy transfers (radiative and non-radiative) either between two ions (activator ion and sensitizer ion) or within the energy states of an activator ion itself in the visible-spectrum range which has been shown in figure 3.2.7a for UCN-dots. For UCN-dots ( $\text{NaYF}_4:\text{Yb}^{3+}; \text{Er}^{3+}$ ) the  $\text{Yb}^{3+}$  ion acts as a sensitizer and  $\text{Er}^{3+}$  acts as an activator.

In fluorescence spectrum (FL) (figure 3.2.7a), the different emissive bands denote the intensity of the emitted higher energy photons at different wave lengths depending on the transfers of electrons from different excited states to the ground state or first excited state. Fluorescence emission spectra of colloidal solutions of UCN-Dots display well separated emissive peaks at room temperature. Only four significant emission bands are identified under the CW-laser excitation source (980 nm).

The energy transfer mechanism has been shown in figure 3.2.7b. The green emissions in between 513 nm to 533 (527 nm,  $E_g = 2.35$  eV) nm and 533 nm- 569 nm (545 nm;  $E_g = 2.28$  eV) can be assigned to the  $2\text{H}_{11/2} \rightarrow 4\text{I}_{15/2}$  and  $4\text{S}_{3/2} \rightarrow 4\text{I}_{15/2}$  transitions, respectively.



**Figure 3.2.7: Fluorescence Spectra of UCN-Dot-colloidal solution in cyclohexane with a 980 nm continuous wave (CW) NIR excitation (Power Density 1000 mW/ cm<sup>2</sup>) exhibiting four significant emission bands at room temperature (b) The relevant energy diagram of dot-sized upconverting nanocrystals and upconversion processes succeeding 980 nm laser-diode excitation. Further it predicted energy transfers (with three direct energy transfers) with their corresponding pathways (c) Three images are with colloidal solutions and showing the visible emissions under 980nm laser CW**

A dominant red emission is observed between 630 nm and 680 nm (663 nm;  $E_g = 1.87$  eV) and can be assigned to a transition  $4F_{9/2} \rightarrow 4I_{15/2}$ . A feeble NIR emission between 795 nm and 883 nm (838 nm;  $E_g = 1.48$  eV) appeared due to the  $4S_{3/2} \rightarrow 4I_{13/2}$  transition of the photons. A highly intense emission band appeared in between 485 nm to 506 nm (496 nm;  $E_g = 2.5$  eV) can be assigned to the transition  $4F_{5/2} \rightarrow 4I_{15/2}$ , which occurs through a direct energy transfer from  $2F_{5/2}(Yb^{3+}) \rightarrow 4G_{11/2}(Er^{3+})$  by continuous 980 nm input excitation laser source. From the higher excited state  $Er^{3+}$  ion can be relaxed to the next lower states following the path

$2H_{9/2} \rightarrow 4F_{3/2} \rightarrow 4F_{5/2}$  (due to close proximity of these intermediate levels) through several non-radiative multiphonon relaxations which do not emit any photons. The emission band appeared in between 485 nm and 506 nm can neither be fallen exactly under green emission band nor to blue emission due to a divergent wavelength range. Therefore, we cannot assign them directly to the transitions  $2H_{11/2}/4S_{3/2} \rightarrow 4I_{15/2}$  or  $2H_{9/2} \rightarrow 4I_{15/2}$ .

An intermediate or reservoir state ( $4F_{5/2}$ ,  $4F_{3/2}$ ) should be responsible for such emissions which can be assigned to the transition  $4F_{5/2} \rightarrow 4I_{15/2}$  (an immediate cross relaxation occurs between  $4F_{3/2}$  and  $4F_{5/2}$  levels due to their close proximity) and follows the energy transfer path:

$2F_{7/2}(Yb^{3+}) \rightarrow 2F_{5/2}(Yb^{3+}) \rightarrow 4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+}) \rightarrow 4F_{3/2}(Er^{3+}) \rightarrow 4F_{5/2}(Er^{3+}) \rightarrow 4I_{15/2}(Er^{3+})$   
 which includes three non-radiative relaxations such as (i)  $4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ , (ii)  $2H_{9/2}(Er^{3+}) \rightarrow 4F_{3/2}(Er^{3+})$  and (iii)  $4F_{3/2}(Er^{3+}) \rightarrow 4F_{5/2}(Er^{3+})$  (figure 3.2.7b).

Nearly 50% absorbed NIR photons are upconverted from the UCN-dots resulting in visible emission spectrum. As the synthesized particles are of dot-sized particles (size~ 3.5 nm), therefore, number of non-radiative relaxations increase by the solvent molecules and an overall quantum yield (Q.Y.) decreases.

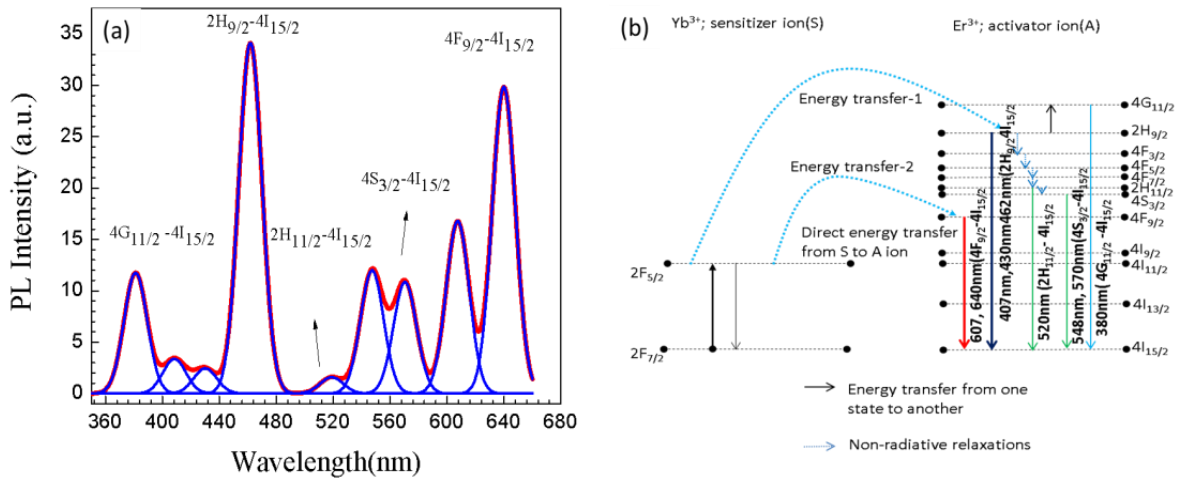
The energy level diagrams of UCN-dots and their up-conversion mechanisms following CW-980 nm laser diode excitation is shown in figure 3.2.7b, where the energy transitions occurred through several radiative and non-radiative emission pathways. As reported earlier, for  $NaYF_4:Yb^{3+};Er^{3+}$  nanocrystals maximum two to three emission bands were obtained from their entire fluorescence spectrum region. However, for our UCN-Dots four significant emission bands have appeared (figure 3.2.7a). The intensity ratios of green emissions from 513 nm-533 nm and 533 nm- 569 nm to red emission from 630 nm-680 nm yielded much higher values (such as 1.75 and 2.67, respectively) compared to the results reported for UCN nanoparticles with larger sizes. In previous reported a size dependent relation of GRR

(intensity ratio of green to red emission) in  $\text{Yb}^{3+}$ ;  $\text{Er}^{3+}$ -co-doped  $\text{NaYF}_4$  nanocrystals and a graphical plot of GRR as a function of particle sizes has also been observed, where the green emission became more pronounced with decreasing particle size. The GRR value of the present UCN-dots appeared to be very high relative to the UCN nanoparticles with larger size. The GRR value of the present UCN-dots appeared to be high compared to the larger sized UCN particles.

This phenomenon can be explained as: the dot-sized UCN particles are responsible for an increased number of non-radiative relaxations as the dot-sized nanoparticles are having higher specific surface area to volume ratio. As a result, an increased number of doped lanthanide ions are closer to their periphery (surface) leading to a greater number of non-radiative relaxations (as shown in figure 3.2.7b with energy–diagram) between their different energy levels. As a result, the overall fluorescence intensity decreases. Please see the image (figure 3.2.7c) for the visible emissions under 980 nm laser-diode excitation sources.

### 3.2.4 Photoluminescence

Figures 3.2.8a and 3.2.8b show the photo luminescence (PL) spectra of UCN-dots in aqueous medium obtained with an excitation wavelength of  $\lambda = 450$  nm and their corresponding energy transitions, respectively. PL bands are observed mostly in visible region (380 nm-700 nm). The obtained major bands are centred at 407 nm, 430 nm, 462 nm, 520 nm, 548 nm, 570nm, 607nm, 640nm following two direct energy transfers from  $\text{Yb}^{3+}$  ion to  $\text{Er}^{3+}$  ion (figures 4a, 4b). NIR-NIR PL was reported for  $\text{NaYF}_4:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  UCNPs elsewhere[30,31]. However, excitingly in the present study visible to visible conversion is observed for UCN-dots while a 450 nm excitation source was used.



**Figure 3.2.8: (a) PL spectra of the UCN-dots of size 3.5 nm. The spectrum was obtained with excitation wavelength of 450nm. The peak positions represent the different transitions of the photons at the visible region (b) energy transitions within electronic states of PL spectra obtained with excitation wavelength of 450nm**

The highest PL emission bands are observed at 462 nm ( $E_g = 2.68$  eV) and at 640 nm ( $E_g = 1.94$  eV) a strong intense emission band is observed. Additionally, few more PL emission bands appeared relatively with weak intensity. From figures 3.2.8a and 3.2.8b the emission band appeared at 520 nm ( $E_g = 2.38$  eV) and can be attributed to the energy transition  $2H_{11/2} \rightarrow 4I_{15/2}$  and other two bands appeared at 548 nm ( $E_g = 2.26$  eV), 570 nm ( $E_g = 2.18$  eV) correspond to the  $4S_{3/2} \rightarrow 4I_{15/2}$  transition and these three are responsible for the green emission. Whereas red emission band appeared at 607 nm ( $E_g = 2.04$  eV) and 640 nm ( $E_g = 1.94$  eV) which is configured for the  $4F_{9/2} \rightarrow 4I_{15/2}$  transition. Emission-bands appeared at ~407 nm ( $E_g = 3.05$  eV), 430 nm ( $E_g = 2.88$  eV), 462 nm ( $E_g = 2.68$  eV) satisfied the energy transition  $2H_{9/2} \rightarrow 4I_{15/2}$ . Interestingly, one band with moderate intensity appeared (in near-UV region) at 380 nm ( $E_g = 3.26$  eV) corresponds to the energy transfer  $4G_{11/2} \rightarrow 4I_{15/2}$  following a transitional energy transfer (indirect energy transfer) from  $2H_{9/2} \rightarrow 4G_{11/2}$ . However, the corresponding emission bands observed

from PL has been compared with fluorescence spectra (FL) obtained with the interaction of CW-980 nm laser and discussed in the subsequent sections.

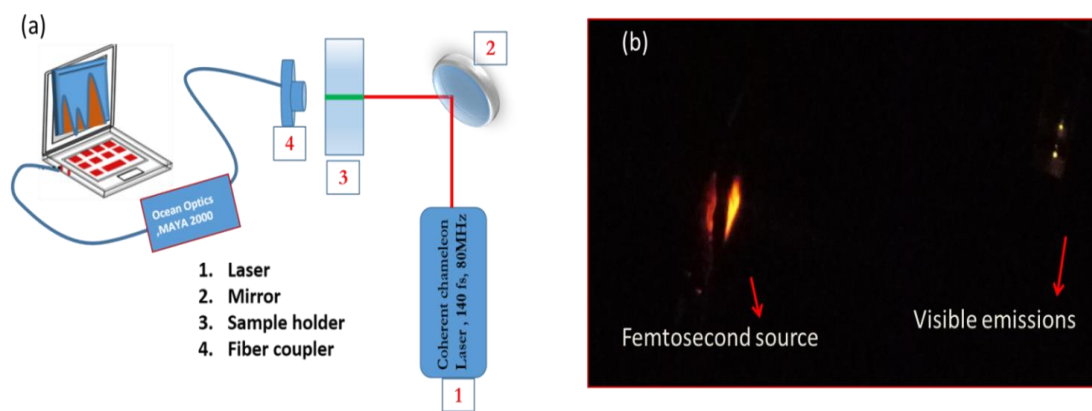
### **3.2.5 Up-conversion due to femtosecond laser (fs-laser) irradiation and High-Power band generation in UV- region**

A Ti sapphire tunable oscillator laser with pulse duration  $\sim 140$  femtoseconds at a repetition rate of 80 MHz (coherent chameleon ultra-II made) was used as a pumping source for sample excitation. Luminescence signal was recorded using non-gated Spectrometer (Ocean Optics, MAYA 2000). The schematic of experimental setup is shown in figure 3.2.9. Luminescence results exhibits the appearance of additional bands in UV region (205 nm-231 nm) other than the appearance of a number of bands in visible region (figure 3.2.10). The generation of emission bands in UV region in interaction with femtosecond pulses is due to non-linear effects introduced by transient second order non-linearity by femtosecond pulses. Further it is noticed that appeared luminescence bands in UV region show clear shifting with respect to the incident pump wavelengths and this phenomenon is reported here for the first time.

Aktsipetrov et .al reported the magnetization induced harmonic generation and THz in Bi:YIG -a magneto photonic crystal[275]. If these samples are subjected to intense beam of laser then higher order optical harmonics are generated. The first shows the linear response due to transmission while strongest non-linear response is attributed to higher order non-linearity. However, all these processes are applicable in case of non-centro symmetrical materials. Most of the materials possess odd order non-linear susceptibility due to broken crystal tractions, defects, external field effects etc. In non-centro symmetry materials the response is from structure, however, in case of nanomaterials, structure relation response become more important and size reduction helps to generate efficient higher order harmonics which is not clear in present study.

The non-linear magneto optical effect could be the reason of getting higher order non-linear response from the UCN-dots and as a result upconversion bands are appeared in UV-region. In figures 3.2.10 (a & b), different emission bands of colloidal UCN-dots have been observed under the excitations of four different incident pump wavelengths, such as  $\lambda = 950$  nm, 960 nm, 970 nm and 980 nm in femtosecond laser (fs-laser) setup (figure 3.2.9). We have observed emissive bands in both of UV and visible regions.

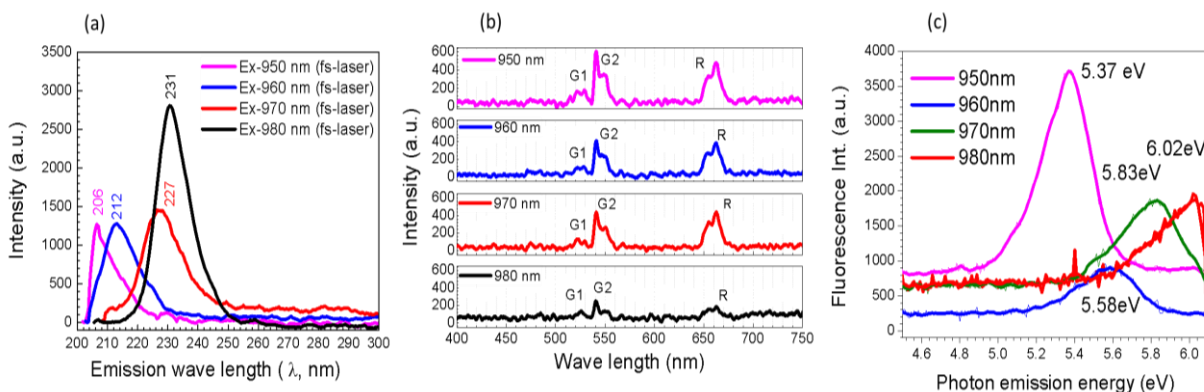
In UV region (1st series of the observed emissive bands) (figure 3.2.10a), at  $\lambda = 950$  nm, 960 nm, 970 nm and 980 nm fs-excitation wavelengths, the emission bands are appeared at 206 nm, 212 nm, 227 nm and 231 nm, respectively. Thus, clear shifting of bands from 206 nm to 231 nm are observed as the excitation wavelength changes from  $\lambda = 950$  nm to 980 nm.



**Figure 3.2.9: (a) Schematic diagram of a complete experimental set up for femtosecond laser study (b) Visible emissions (right) with femtosecond laser source (left) during experiment**

Further, a number of emissive bands also appeared in visible region (figure 3.2.10b). These emissive bands in visible region are appeared with lesser intensity compared to those appeared in UV region but still their intensities are significant enough to consider. At four different excitation wavelengths 2nd series of emissive bands (G1) are appeared in the wavelength range between 506-535 nm with highest band positions at 521 nm, 522 nm, 522

nm and 524 nm along with 3rd series of bands (G2) appeared between 536 nm-562 nm containing highest positions at 540 nm, 540 nm, 541 nm and 542 nm for 950 nm, 960 nm, 970 nm and 980 nm excitations, respectively.



**Figure 3.2.10: (a) Up-conversion Luminescence spectra in the UV-region (on excitation with fs-laser), exhibited red shifting with increasing excitation wavelengths (b) Up-conversion Luminescence spectra at the visible region for different fs-laser excitations (c) Band gap energies received from different fluorescence spectra under different excitation fs-laser sources**

Thus, in visible region maximum of 2 nm band shifting has been observed. Further, 4th series of emissive bands (in visible region) are appeared in between 643 nm-677 nm having highest intense positions at 662 nm, 662 nm, 662 nm and 663 nm under fs-laser irradiation sources 950, 960, 970 and 980 nm, respectively and not comprised any significant shifting with change in irradiation wave lengths (figure 3.2.10b).

Thus, main interesting attraction is the emission in UV region once the UCN-dots are excited under fs-laser and their remarkable red shifting once they are excited from 950 nm to 980 nm fs-laser irradiation (figure 3.2.10a). It is very exciting that there is no shifting of band positions observed in the visible region for G1, G2 or R bands (figure

3.2.10b). Moreover, bands appeared in UV region exhibits noticeable red shifting as  $\lambda$  increases from 950nm to 980nm irradiation (figure 3.2.10a).

This exciting phenomenon can be explained by calculating the number of photons absorbed under fs-laser excitation, which is further strongly dependent on:

- (i) fs-laser power and number of excited photons
- (ii) the shifting of band gaps ( $E_g$ = band gap energy). To measure fs-laser power dependent luminescence and the number of absorbed photons taken part in the process, one power law concept has been used to be

$$I_{uc} \sim I_{fs}^n \quad (1)$$

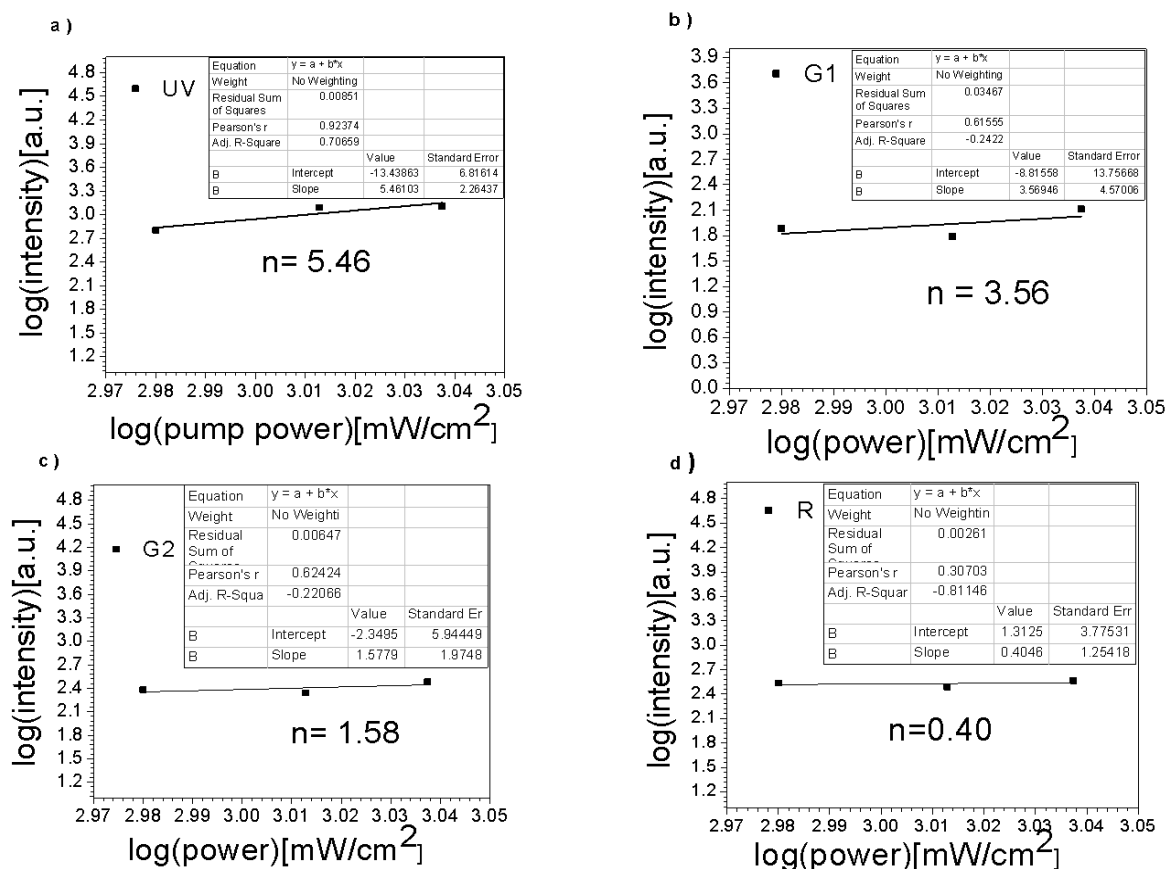
Where  $I_{uc}$  is the luminescence intensity which is proportional to ' $n^{th}$ ' of excitation power  $I_{fs}$ , ' $n$ ' is the number of absorbed photons per photon emitted under fs-laser excitation power  $I_{fs}$  and this has been calculated from the slopes of  $\log(I_{uc})$  versus  $\log(I_{fs})$ (figure 3.2.11).

Similar power law concept has been used to calculate NIR laser power dependent luminescence using NIR elsewhere[276]–[280]. It can be noticed that, for G1 and G2 luminescence bands we need to transfer a minimum pair of photons ( $n = 2$ ) from one sensitizer ion i.e. from  $Yb^{3+}$  (donor ions) to one activator ion i.e. to  $Er^{3+}$  (acceptor ions) (1: 1 molar ratio) under fs-laser (NIR) excitations [277]–[279].

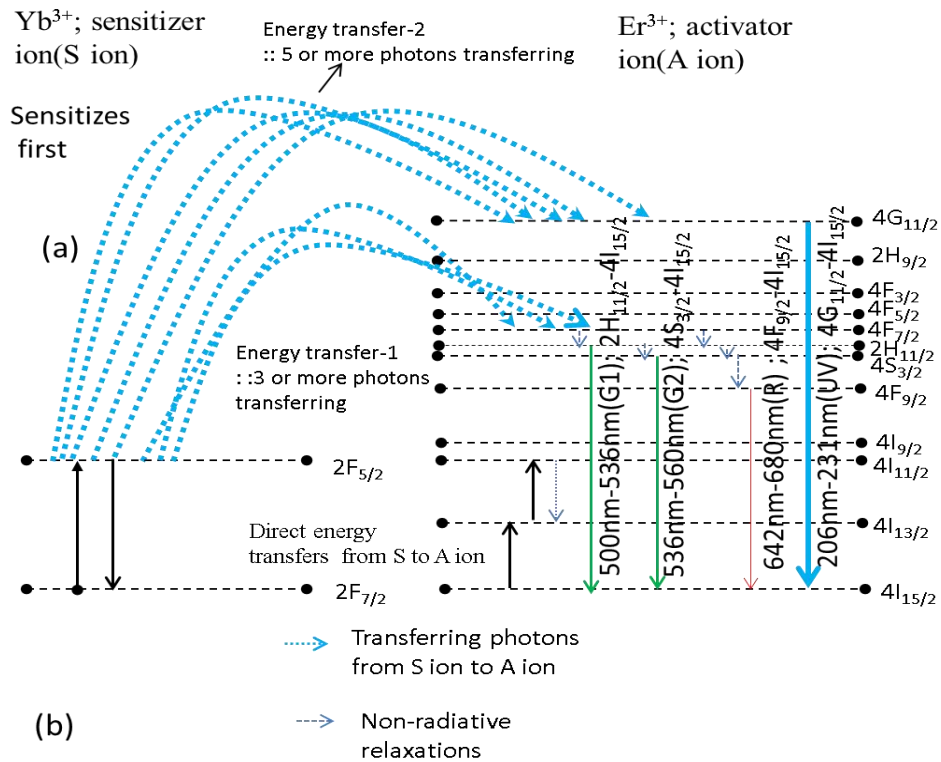
The values obtained to be  $n(G1) = 3.6$  and  $n(G2) = 1.6$ , respectively (figures 3.2.11b), 3.2.11c; ( $\log(I_{uc})$  versus  $\log(I_{fs})$  plots). Further, the number of absorbed photons for UV and red- emissions have also been calculated and found to be  $n(UV) = 5.46$  and  $n(R) = 0.40$ , respectively (figures 3.2.11a, 3.2.11d). Highest value of " $n$ " for UV (5.46) satisfies the highest number of transferred photons compared to the other emissions. The relative energy transfers for UCN-Dots in UV-Vis region are occurred due to the

high-power fs laser and their significant relevance along with corresponding excitation path ways can be explained as:

By fs-laser excitation sources (980, 970, 960 and 950 nm), initially the  $\text{Yb}^{3+}$  sensitizes and excites to  $2F_{5/2}$  level and transfers energy to  $\text{Er}^{3+}$  in order to excite them in different energy levels e.g.  $4I_{13/2}$ ,  $4I_{11/2}$ ,  $4F_{9/2}$ ,  $4F_{7/2}$ ,  $4G_{11/2}$ (figure 3.2.12a).



**Figure 3.2.11: Dependence of Up-conversion luminescence intensity on fs-Laser power for (a) deep-UV , (b) Green G1(c ) Green G2 and (d) Red (R) related emission (excited fs-laser), respectively. The number of absorbed photons per photon emitted under the fs-laser excitation power “n” value determined for the deep-UV, G1, G2 and R emissions for UCN-dot and their values also mentioned in the respective plots.**



**Figure 3.2.12: (a) Energy band diagram (energy transitions) under femtosecond laser source and (b) visible emissions in sample-cuvette during experiment (images are taken with five observations).**

Population of  $4I_{11/2}$  energy-level occurs by transferred energy from  $2F_{5/2}$  ( $\text{Yb}^{3+}$ ) level. There are two ways to populate  $4I_{13/2}$  ( $\text{Er}^{3+}$ ) level; notably one is absorbing a 980 nm/or 970 nm/or 960 nm/or 950 nm photon from  $4I_{15/2}$  ( $\text{Er}^{3+}$ ) energy state; another one is by

non-radiative relaxation ( $4I_{11/2} \rightarrow 4I_{13/2}$ ) between  $4I_{11/2}$  and  $4I_{13/2}$  energy levels. A direct energy transfer (designated as energy transfer 1) can be populated to  $4F_{7/2}$  level from which non-radiative relaxations occurs to  $2H_{11/2}$  level and further to  $4S_{3/2}$  level, both of which are responsible for green emissions (G1 and G2, figure 3.2.10b, 3.2.12a) following the sequence path:

$2F_{7/2}(Yb^{3+}) \rightarrow 2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}/4S_{3/2}(Er^{3+}) \rightarrow 4I_{5/2}(Er^{3+})$  which includes one and/or two non-radiative relaxations such as  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}$  and/or  $2H_{11/2} \rightarrow 4S_{3/2}(Er^{3+})$ .

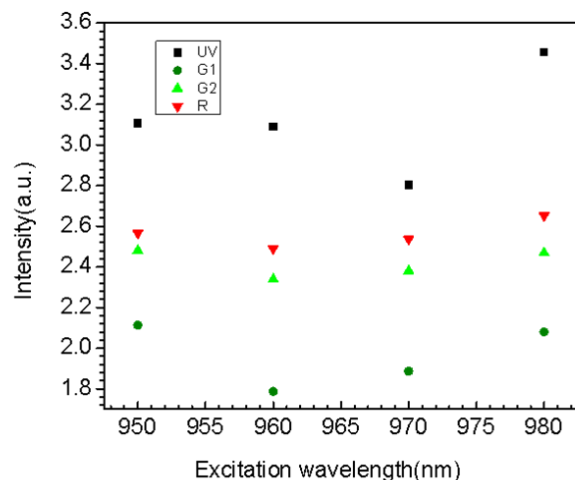
The corresponding energy transitions for G1 and G2 emissions bands are  $2H_{11/2}-4I_{15/2}$  and  $4S_{3/2}-4I_{15/2}$ , respectively. The second direct energy transfer (energy transfer 2) occurs from  $2F_{5/2}(Yb^{3+}) \rightarrow 4G_{11/2}(Er^{3+})$  level by continuous high-power input excitation laser- source. From higher excited state ( $4G_{11/2}$ ),  $Er^{3+}$  ion can be relaxed directly to the ground state ( $4I_{15/2}$ ) with emitting high intense ultraviolet (UV) emissions corresponding to transition  $4G_{11/2} \rightarrow 4I_{15/2}$  without experiencing any kind of a non-radiative relaxations.

$$\text{Energy transfer 1: } 2F_{7/2}(Yb^{3+}) + 4F_{7/2}(Er^{3+}) \rightarrow 2F_{5/2}(Yb^{3+}) + 4I_{11/2}(Er^{3+}) \quad (2)$$

$$\text{Energy transfer 2: } 2F_{7/2}(Yb^{3+}) + 4G_{11/2}(Er^{3+}) \rightarrow 2F_{5/2}(Yb^{3+}) + 4F_{9/2}(Er^{3+}) \quad (3)$$

The moderate red emission (R) assigning to the  $4F_{9/2} \rightarrow 4I_{15/2}$  transition appears following the path:  $2F_{7/2}(Yb^{3+}) \rightarrow 2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2} \rightarrow 4S_{3/2}(Er^{3+}) - 4F_{9/2}(Er^{3+}) \rightarrow 4I_{15/2}(Er^{3+})$  including three non-radiative relaxations such as  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}$ ,  $2H_{11/2} \rightarrow 4S_{3/2}(Er^{3+})$  and  $4S_{3/2}(Er^{3+}) \rightarrow 4F_{9/2}(Er^{3+})$ . Thus, there are total two direct energy transfers occurred and they become responsible for UV and visible (G1, G2 and R) emissions which can be written in terms of the following two equations (equations 2 and 3 ;figure 3.2.12) considering the match of energy separation [281].

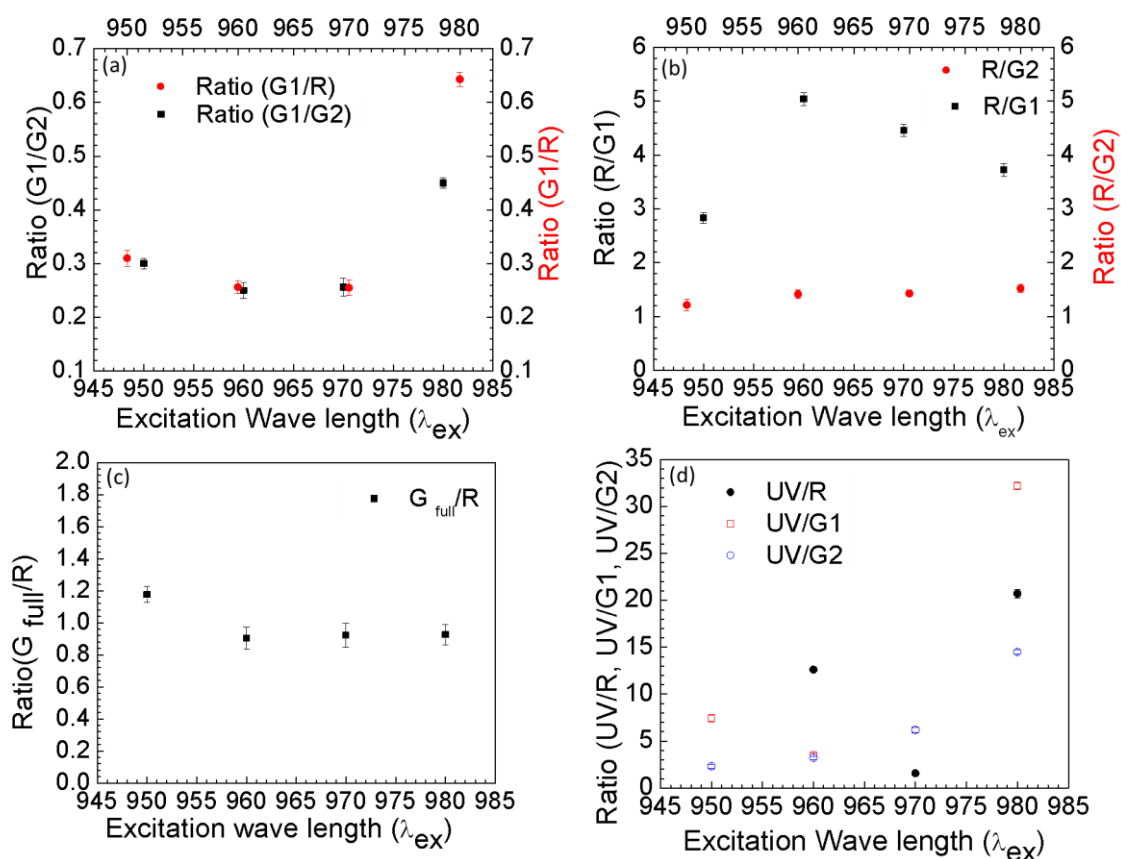
It can be noted that there is no significant change in band positions for G1, G2 or R observed with change in the fs-laser excitation wave lengths (950 to 980 nm) (figure 3.2.10), however change in intensity is observed (figure 3.2.13) with change in the excitation wave lengths.



**Figure 3.2.13: Plots intensity [a.u.] vs excitation wavelength [nm] for UV, G1, G2, R**

A noticeable change in band intensities and their relative ratios with different excitations for (i) peak ratio (G1/G2) and (G1/R) (figure 3.2.14a), (ii) peak ratio (R/G1) and (R/G2) (figure 3.2.14b), (iii) peak ratio ( $G_{full}/R$ ) (figure 3.2.14c) and (iv) peak ratio (UV/G1), (UV/G2) and (UV/R) (figure 3.2.14d) have been observed in figure 3.2.14. These phenomena have been observed due to different efficient population causes from the effective number of excited photons, i.e.,  $n(UV)$ ,  $n(G1)$ ,  $n(G2)$  and  $n(R)$  (figure 3.2.11). The fractional number of absorbed photons for red emission  $n(R)$  (actual 0.40) signifies that red emission has been occurred only due to the cross-relaxation of photons from the higher energy state ( $4F_{7/2}$ ) to the lower energy state ( $4F_{9/2}$ ) and not due to any other direct energy transfers.

However, the appearance of strong emission bands in UV region can be explained with the change of  $E_g$  values received due to the interaction with fs-laser.  $E_g$  values for different UV- bands have been calculated from fs-luminescence spectra using the method reported elsewhere [39,40] and found to be 5.37, 5.58, 5.83 and 6.02 eV (figure 3.2.10c).



**Figure 3.2.14:** (a-d) Plots for peak ratios vs excitation wavelengths (nm) (a) G1/R, G1/G2 vs  $\lambda_{ex}$  (b) R/G1, R/G2 vs  $\lambda_{ex}$  (c) G<sub>full</sub> vs  $\lambda_{ex}$  (d) UV/G1, UV/G2, UV/R vs  $\lambda_{ex}$

**Table 3.2.2: Band Gap Energy ( $E_g$ ) of UCN-dots with different excitation photon energies (Fs) and single photon energy (FL, PL)**

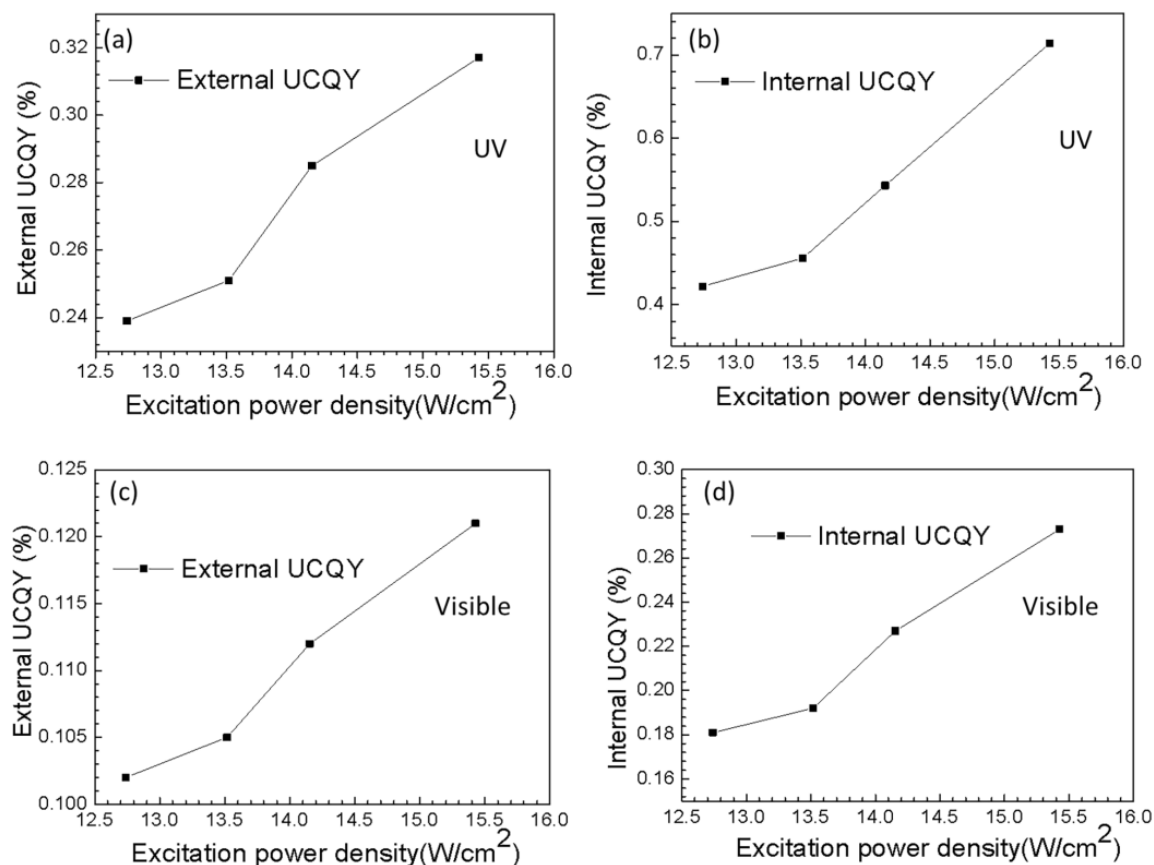
| Types of Spectra              | Excitation Wavelength $\lambda_{ex}(nm)$ | Excited photon energy (eV) [1240/Wavelength] | Band gap values(eV)                                                    |
|-------------------------------|------------------------------------------|----------------------------------------------|------------------------------------------------------------------------|
| Femtosecond Laser(Fs)-spectra | 950nm                                    | 1.31eV                                       | 5.37eV                                                                 |
|                               | 960nm                                    | 1.29eV                                       | 5.58eV                                                                 |
|                               | 970nm                                    | 1.28eV                                       | 5.83eV                                                                 |
|                               | 980nm                                    | 1.27eV                                       | 6.02eV                                                                 |
| Fluorescence-spectra(FL)      | 980nm                                    | 1.27eV                                       | 2.5eV, 2.35eV, 2.28eV, 1.87eV, 1.48eV                                  |
| Photoluminescence spectra(PL) | 450nm                                    | 2.76eV                                       | 3.26eV, 3.05eV, 2.88eV, 2.68eV, 2.38eV, 2.26eV, 2.18eV, 2.04eV, 1.94eV |

Hence, clear red shiftings have been observed with increasing excitation wave lengths. It can be noted that the fitting procedure has been done with highest band energy values which corresponds to  $E_g$ . Therefore, the shifting of bands in UV region with change in fs-laser excitations is obvious. Further, the excited photon energy corresponding to the fs-laser excitations have been calculated and found to be 1.30, 1.29, 1.27 and 1.26 eV (table 3.2.2).

Detailed result of excited photon energy and corresponding  $E_g$  values with respect to excitation wavelengths for 980nm ex.- fluorescence (figure 3.2.7), photoluminescence (figure 3.2.8) and fs-luminescence (figure 3.2.10 and figure 3.2.12) are provided in tabulated form (table 3.2.2).

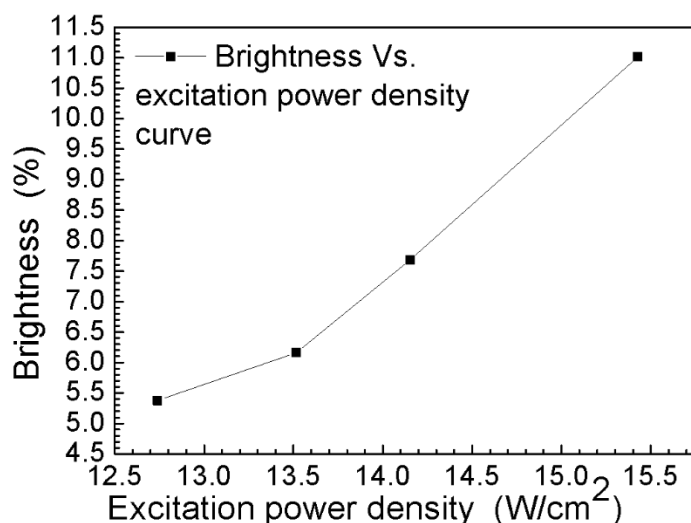
Further, power dependent luminescence properties have also been investigated from figure 3.2.10 and a sharp red sifting is observed for UV emission bands with

decreasing incident powers of 1.09 W, 1.00W, 0.955W, and 0.900W for 950nm, 960nm, 970nm and 980nm irradiations, respectively. To find out the quality of the synthesized UCN-dots of  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ , from the excited power densities of  $15.428 \text{ W/cm}^2$ ,  $14.154 \text{ W/cm}^2$ ,  $13.517 \text{ W/cm}^2$ , and  $12.739 \text{ W/cm}^2$  the UCQYs have been calculated according to the method reported elsewhere [284], [285] and the values are shown in figure 3.2.15.



**Figure 3.2.15: (a) and (b) Show the External-UCQY (%) and Internal-UCQY (%) with excitation power density for emission in UV regime, respectively; (c) and (d) show External-UCQY (%) and Internal-UCQY (%) with excitation power density for the emission in visible regime, respectively for UCN-dots of  $\text{NaYF}_4:\text{Yb}^{3+}:\text{Er}^{3+}$**

However, in the present study for UCN-dot, for visible emissions under fs-laser system both external and internal UCQY. have been calculated according to the method reported elsewhere [284], [285] and found to be (External-UCQY):  $0.121 \pm 0.003 \%$ ,  $0.112 \pm 0.002 \%$ ,  $0.105 \pm 0.001 \%$ ,  $0.102 \pm 0.002 \%$ ; and (Internal-UCQY):  $0.273 \pm 0.004 \%$ ,  $0.227 \pm 0.002 \%$ ,  $0.192 \pm 0.002 \%$ ,  $0.181 \pm 0.005 \%$ ; whereas in UV-region they are calculated to be (External-UCQY):  $0.317 \pm 0.003 \%$ ,  $0.285 \pm 0.004 \%$ ,  $0.251 \pm 0.002 \%$ ,  $0.239 \pm 0.002 \%$ ; and (Internal-UCQY):  $0.714 \pm 0.007 \%$ ,  $0.543 \pm 0.002 \%$ ,  $0.456 \pm 0.001 \%$ ,  $0.422 \pm 0.001 \%$  under excitation pump powers 1.09 W, 1.00W, 0.955W, and 0.900W, respectively and appear to be efficient for “d” < 4nm UCN-dots while compared with as-said previous observations [284]–[287]. We have observed that UCQY increases with increase in the irradiance. The corresponding UCQY vs. excitation power density results are represented in figure 3.2.15 and brightness vs. excitation power density results for UV emission is shown in figure 3.2.16. Thus with increasing power density both the internal and external UCQY values have increased.



**Figure 3.2.16: Brightness (w.r.t internal Q.Y. in UV emission) vs excitation power density curve**

It can be noted in this line that Boyer et al. reported the UCQY for different sizes of UCNPs ( $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ ) and their values were 0.005%, 0.10%, 0.30% and 3% for 8-10nm, 30nm, 100nm and above 100nm sized UCNPs, respectively, once they were excited with 980 nm NIR laser [286]. Chen et al. reported the UCQY values of 0.13%, 0.07%, 0.05% and 0.95% under 540, 660, 800, and 970 nm NIR excitations, respectively for the UCNPs of size 100 nm ( $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ ) [284]. In another study the internal UCQY for core shell UCNPs of size  $\sim 40$  nm ( $\beta\text{-NaYF}_4:\text{Er}^{3+}$  core, dia. 19.2 nm and  $\beta\text{-NaLuF}_4$  shell with thickness 18.8 nm) was reported as 3% with 1523 nm NIR laser irradiance [285]. Therefore, it can be concluded that the UCN-dots reported in present work exhibited higher UCQY in fs-laser radiation with respect to the UCNPs ( $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ ) reported in the earlier works.

However, advent of ultrafast (UF) lasers has revolutionized the field nonlinear optical in-centro-symmetry and non-centro-symmetry materials. Electro-optic (E-O) and nonlinear phenomena are realized in materials under the influence of strong electric field and popularly known as Pockels and Kerr effects [288]. Nonlinear phenomena are observed due to the introduction of birefringence by external E-M field and attributed to change in refractive index. The generation of high-power energy upconversion from UCN-dots can be occurred either from the surface or interfaces of the particles. The generation of high-power upconversion emission completes in three steps, namely, first, (i) incident beam of intense UF radiation induced change in birefringence or refractive index in the materials, then (ii) the UCN-dots behave like a nonlinear hertzian oscillator and generates polarized waves from the surface or interfaces and finally (iii) the generated polarized waves interact with each other. The interference of polarized waves generates the high energy upconversion from UCN-dots.

### 3.2.6 Summary and Conclusions of PART II:

NIR to visible upconversion luminescent UCN-dots with cubic phases ( $\text{NaYF}_4$ :  $\text{Yb}^{+3}$ ;  $\text{Er}^{+3}$ ) were synthesized by solvo- thermal decomposition of lanthanide hexahydrate precursors with organic solvents following a novel and straight forward synthesis approach. The average particle size obtained to be 3.4 nm in dia. which are smallest in size reported ever and stable for a minimum of one year with upconversion luminescence. This work further revealed the emission of UV luminescence under interaction with femtosecond laser. Though, owing to their very small sizes, the gross amount of fluorescence intensity was reduced as a large number of cross relaxations were induced during energy-transfer mechanism but still they showed very special property while interacting with femtosecond laser. Importantly, this work revealed that the UCN-dots could be a great potential candidate for emitting highly efficient ultraviolet radiation and useful as UV-emitting nanophosphors which can be used in several bio-applications[289]. Since various bio-applications of UCNPs have already been reported, therefore this work directs us that the unique sizes (3.4 nm) of the UCN-dots could further open a domain of new possibilities in biomedical engineering and medical-fields for improving the treatments of infected cancer cell and tumour cells along with improving the efficiency of several devices where the non-linear optical activities play an important role.

### 3.2.7 Calculation part of number of unit cells present in single UCN-dot:

The number of unit cells in UCN-dot:

The average lattice constant has been found to be = 5.39 Å

Assuming,

UCN-dots to be almost spherical, the volume of one particle has been calculated as  
$$= V_{\text{UCN-dots}} = \frac{4}{3} \times 3.14 \times (1.75)^3 = 22.4379 \text{ nm}^3$$

[Considering average particle diameter as 3.5nm, radius= 3.5/2= 1.75nm]

Now,

As the crystal structure is cubic-FCC, UCN-dots consist of cubic unit cells, so the volume of the cubic unit cell =  $V_{\text{unit cell}} = (a_c)^3 = (5.39\text{\AA})^3 = 156.590 \times 10^{-3} \text{ nm}^3$ .

Therefore,

The number of unit cells in one UCN-dot particle =  $V_{\text{UCN-dots}}/V_{\text{unit cell}} = 0.143 \times 10^3 \sim$  almost 143 no. of unit cells.

Note:

In cubic cell, Number of  $\text{F}^-$  ions = 8, so in one particle 1144 no. of  $\text{F}^-$  ions are present.

Number of  $\text{Na}^+/\text{RE}^{3+}$  ions = randomly occupy the positions

According to previous study, please follow the link <http://dx.doi.org/10.1101/114744>

As standardized calculation, with rare earth dopants ( $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ ), number of effective Na, F, Yb, Er atoms present are= 2, 8, 1, 1 as fraction of  $\text{Y}^{3+}$  ions are substituted by rare earth ions( $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ ) [ref-as mentioned above]

## **Chapter 3 RESULT AND DISCUSSION**

# **PART-III**

### **3.3 (Part-III): Self-assembled pearl necklace patterned-upconverting nanocrystals with highly efficient blue and ultraviolet emission: femtosecond laser based upconversion properties**

**Outcome:** Monami Das Modak, Ganesh Damarla, Somedutta Maity, Anil K. Chaudhary and Pradip Paik; Self-organized dendritic-upconverting nanocrystals with highly efficient blue and ultraviolet emission: femtosecond laser based upconversion properties; Published in RSC Advances Journal.

### 3.3.1 Introduction:

Dendrimers are attractive due to several unique properties and for their applications in materials, materials science, industrial applications for designing solar cells, sensors etc. and for biomedical medical applications.[290][291] Rare-earth upconverting materials have been demanded as they are the best energy upconverting (NIR-to-visible) materials ever known, therefore recently researchers are focusing on their design, synthesis and spectroscopic properties. Further, upconverting materials possess potential uses in biological labelling and bio-assays and their extent of uses are increasing remarkably with time [34], [95], [292]–[294]. All these unique features drive us to synthesize dendritic UCNPs having strong upconversion emission. To the best of our knowledge, dendritic UCNPs are never known. A report was found where UCNPs were impregnated in porphyrin dendrimers [295]. In this work we are enabled to prepare dendritic UCNPs in in-situ condition without incorporating any external polymeric dendrimers. The as-prepared UCN-Ds have been formed by consuming all precursors into solid crystal nuclei as white precipitates at lower reaction temperature and then with increasing the reaction temperature crystal growth occurred followed by the formation of dendrimers. The as-prepared dendritic-UCNPs have excellent dispersibility in non-polar solvent (e.g., cyclohexane) and are stable for more than a year. As UCN-Ds exhibit excellent upconversion emission under 980 nm NIR excitation source and 140 femtosecond pulse duration at 80 MHz repetition rate, there is a vast ambit for using them in complex bio-labelling by tuning their spectral properties. Further, for present available systems there are several draw backs in achieving good efficiency for the DNA detection,[296] bio-imaging,[297] sensors and fluorophores,[11], [298], [299] analytes and several other important biomedical applications such as for the treatment of cancers[112], [300]–[302] which can be improved by using UCN-Ds.

Self-assembled materials can be obtained from nature to the laboratory. Self-assembly in living system is biologically controlled whereas; self-assembly formation in laboratory is controlled artificially. The assembly of nanomaterials is purely represented by non-covalent bonding and controlled both by kinetic and thermodynamically. Inside laboratory self-assembly processes are used for designing the artificial nanostructures, such as for assembling proteins, peptides, nucleotides, supramolecular biopolymers etc. and they have myriad applications in biomedical for developing artificial membranes and for various biofunctions [303]–[305]. Self-assembly of various inorganic (metals/hybrids) nanoparticles is well known [306]–[308]. The formation of self-assembled dendritic nanostructures is very much interesting in the area of modern nanotechnology. Dendritic nanostructure of UCNP can exhibit unique properties with their associated building blocks (nanoparticles below 10 nm). The self-assembled architectures of nano sized UCNP can offer a potential platform for future applications, especially in nonlinear optical property based nanotechnology. Dendrimers have become the most exciting nanometre-sized branched architectures, which are formed by repeating nanoscopic building blocks. Hence, the effort of forming such self-assembled dendritic UCNP can be considered as spontaneous assembly of branched building blocks of nanoparticles. Usually, the interactions between the molecules associated with dendritic network structures can be referred to the supramolecular chemistry [309], where non-covalent interactions play major roles between molecules.

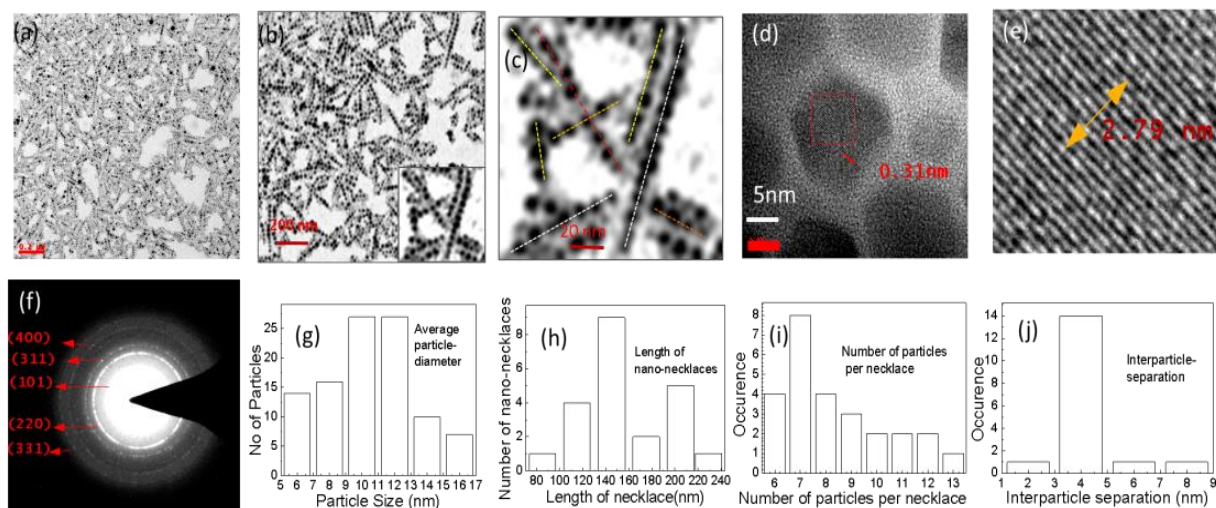
In the above line, present work is focused on the synthesis of self-assembled UCNDs and their upconversion behavior. The upconversion luminescence of self-assembled dendritic UCNP are interesting which have been studied here. In a set of experiments, the upconversion behaviors of UCNDs have been studied with Femtosecond (Fs) Laser (140-femtosecond pulse duration at 80 MHz repetition rate) along with CW-980nm NIR. Further, visible-to visible upconversion has also been studied. The NIR to UV/vis upconversion properties also is observed for UCNDs which is represented

here in detail. At the end, probable mechanisms for the visible-visible/CW-980 NIR/Fs-laser based upconversions with energy band diagrams for different emissions have been elucidated.

### **3.3.2 Experimental observations:**

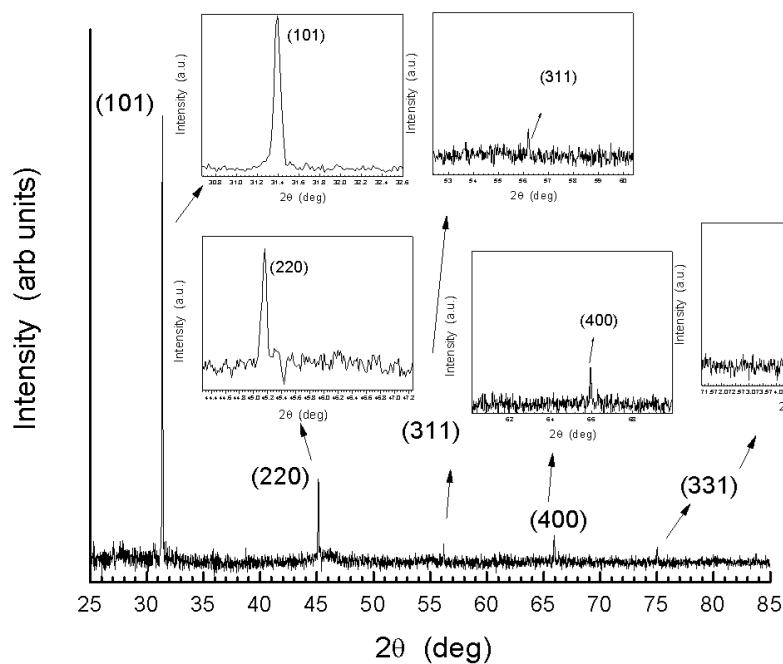
The self-assembly of dendritic network formations and sizes of the as-prepared UCNPs have been shown in figures 3.3.1a - 3.3.1d with different magnification TEM images. TEM was performed using the colloidal solution of UCN-Ds on copper grid (200 mesh, carbon coated). Figures 3.3.1a - 3.3.1c confirm the self-assembled dendritic network formations of synthesized UCN particles. TEM images (figures 3.3.1a, 3.3.1b, 3.3.1c) show the caterpillar-like/pearl chain type necklace formations at different magnification. In-set of figure 3.3.1b clearly shows the density of the particles for different chains. In figure 3.3.1c, lengths of the chains have been shown clearly, where the dotted lines with different colour have been drawn for different chain lengths. Further, it can be noted that the chains are formed with a single row of nanoparticles without overlapping and the distance between two adjacent particles are nearly constant. Most of the regions throughout the sample are able to contain a uniform size of the particles. Overlapping between the particles is almost negligible due to the possible electrostatic interactions.

The high crystallinity is confirmed by high resolution TEM images. Figures 3.3.1d and 3.3.1e show a clear lattice fringes with inter- fringes  $d$  of 0.31nm. The crystalline nature of the UCN-Ds further has been confirmed through the XRD analysis (shown in subsequent section). Figure 3.3.1f shows the SAED pattern with clearly visible ring type diffraction pattern.

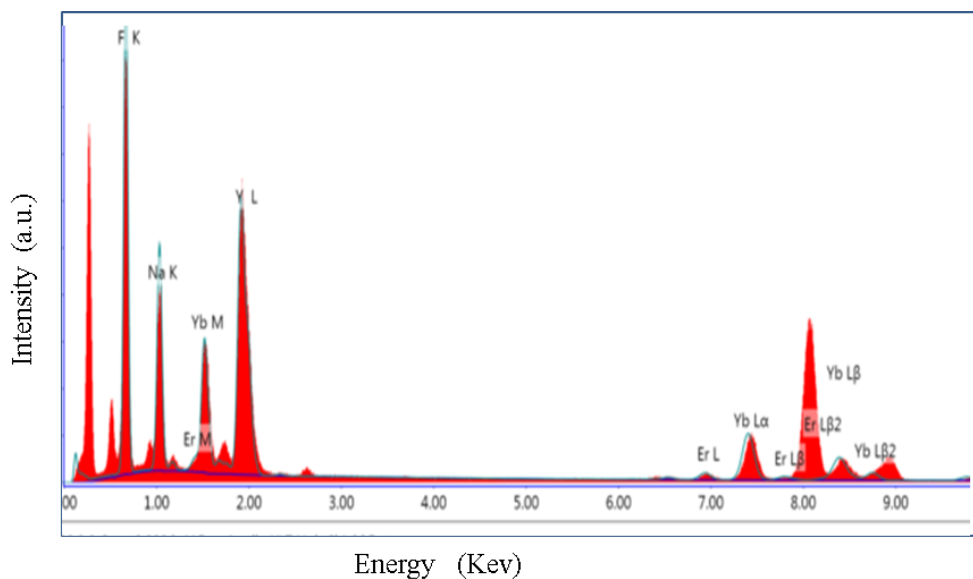


**Figure 3.3.1: TEM images of the synthesized colloidal-dendritic UCNP-Ds at different magnifications. Panels: (a,b)= 200nm, inset in panel (b) shows the clear formation of dendrimers (c) = 20nm, (d),(e) = High resolution micrograph showing lattice fringes, (f)=SAED ring pattern, Histogram of (g)= particle diameter, (h) nano-necklace length, (i) total number of particles per necklace, (j) interparticle-separation**

Figure 3.3.1f has further confirmed five diffraction planes such as (101), (220), (311), (400) and (331) which correspond to the formations of  $\alpha$ - and major  $\beta$ -NaYF<sub>4</sub> UCNP-Ds. Figure 3.3.1g represents the average particle diameter and its distribution is found to be average c.a., 10nm $\pm$ 1 nm. Further, the length of nanonecklaces, number of particles per necklace and interparticle separation has also been calculated from TEM results. From figure 3.3.1h, figure 3.3.1i, and figure 3.3.1j, it can be confirmed that the average nanonecklace length of 140nm which consists of 7-13 numbers of particles per necklace and interparticle distance observed to be c.a. 4nm. X-ray diffraction study was performed to confirm the solid state crystalline structure and is shown in figure 3.3.2. The peak positions that appeared are corresponding to the diffraction planes (101), (220), (311), (400) and (331) respectively. The d-spacing values have also been calculated and found to be 2.9Å, 2.0Å, 1.63Å, 1.43Å and 1.26Å, respectively, which are matching for the  $\alpha$ -/ $\beta$ -NaYF<sub>4</sub> crystalline phases for UCNP-Ds [8], [254], [310]. The



**Figure 3.3.2:** XRD study of synthesized UCN-Ds confirms the crystalline structure. Insets show the observed peaks with their corresponding crystalline planes according to JCPDS-028-1192



**Figure 3.3.3:** EDXA spectrum of UCN-Ds confirming the presence of elements

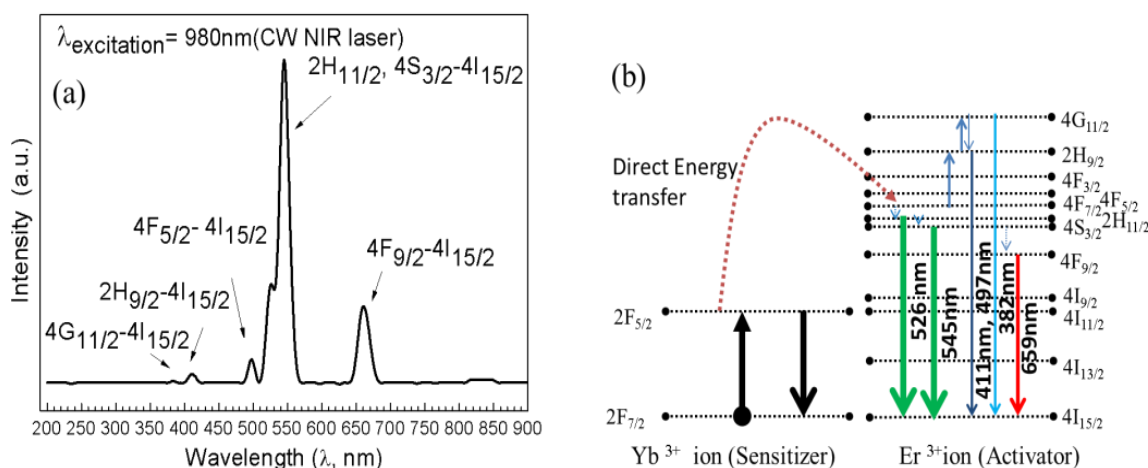
elemental analysis was performed through the Energy Dispersive X-ray Analysis (EDXA) (figure 3.3.3) and confirms for the presence of the elemental Na, Y, F, Er and Yb (table 3.3.1.).

**Table 3.3.1: Elemental compositions observed in EDAX spectrum**

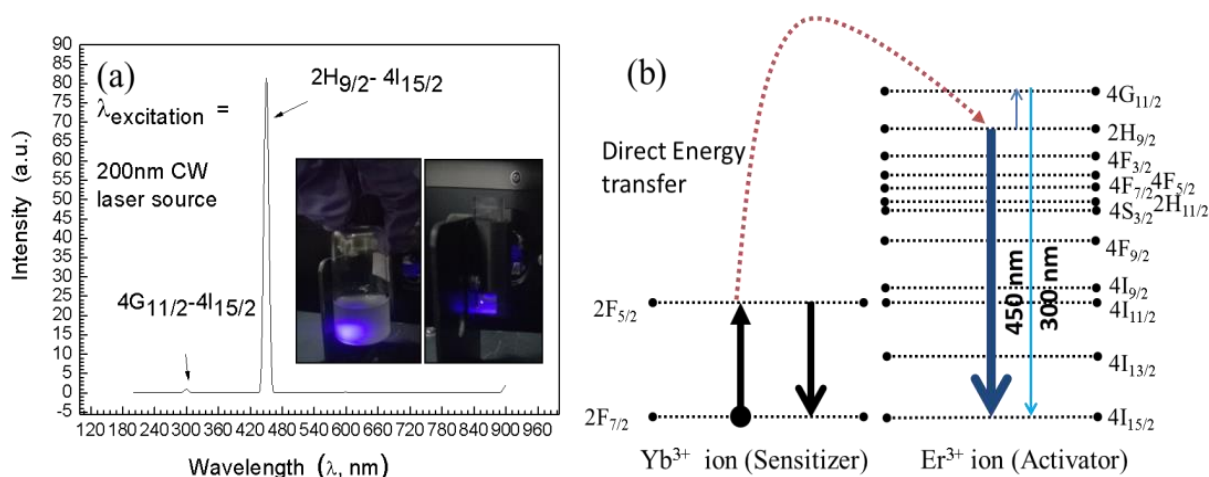
| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| F       | 44.79      | 49.97      |
| Na      | 54.05      | 49.83      |
| Er      | 0.11       | 0.01       |
| Yb      | 0.62       | 0.08       |
| Y       | 0.42       | 0.1        |

The upconversion fluorescence spectrum for UCN-Ds under 980nm NIR CW laser-excitation source is shown in figure 3.3.4. During experiment the power density was maintained to 1000 mW/cm<sup>2</sup>. From figure 3.3.4, it can be observed that UCN-Ds exhibited a very strong upconversion emission. Intense Emission bands with their maximum positions are appeared at  $\lambda = 526\text{nm}$ , 545nm and 659nm for the green emission (G), which are much higher in intensity (4.3 times) than that of the red emission band (R). Green emissions band appeared at 526 nm between 509nm and 531nm and at 545nm between 532nm and 570nm are attributed to the transitions in the energy levels-  $2H_{11/2}$ ,  $4S_{3/2}$  (excited energy levels) and  $-4I_{15/2}$  (ground state energy level of  $\text{Er}^{3+}$  ion), respectively, through a direct energy transfer mode from sensitizer ion ( $\text{Yb}^{3+}$ ) to activator ion ( $\text{Er}^{3+}$ ). A less intense (compared to the green emission) red emission bands at 659nm (between 632nm-691nm) has appeared with  $4F_{9/2}$  to  $4I_{15/2}$  energy transfer which follows a less population in  $4F_{9/2}$  energy level through the energy transfer path  $4I_{13/2} \rightarrow 4F_{9/2}$ . Herein,  $4I_{13/2}$  level is populated with non-radiative

relaxations between  $4I_{11/2}$  and  $4I_{13/2}$  energy levels. Further, very weak emission bands are observed at  $\lambda = 382\text{nm}$ ,  $411\text{nm}$  and  $497\text{nm}$  corresponding to the energy transition modes,  $4G_{11/2}/2H_{9/2} \rightarrow 4I_{15/2}$  and  $4F_{5/2} \rightarrow 4I_{15/2}$ , respectively. These weak emission bands are observed owing to the continuous of input source which excites the  $\text{Er}^{3+}$  ions sequentially to the next higher energy levels following the path  $4I_{15/2} \rightarrow 4I_{11/2} \rightarrow 4F_{7/2} \rightarrow 4G_{11/2}$ . It can be noted that, indirect energy transfers and cross relaxations resulted in very weak emission bands [254], [281]. It also can be noted that, for UCN particles ( $\text{NaYF}_4, \text{Yb}^{3+}; \text{Tm}^{3+}$ ),  $\text{Tm}^{3+}$  ion is responsible for blue emission ( $440\text{nm}$ - $500\text{nm}$ ), [254] following the energy transition paths,  $1D_2 \rightarrow 3F_4$  and  $1G_4 \rightarrow 3H_6$ . However, for our UCN-Ds, without introducing  $\text{Tm}^{3+}$  precursors we are able to achieve high intense blue emission which could be helpful as blue emitting nanophosphors and can be effective for designing biomedical devices and applications [311].



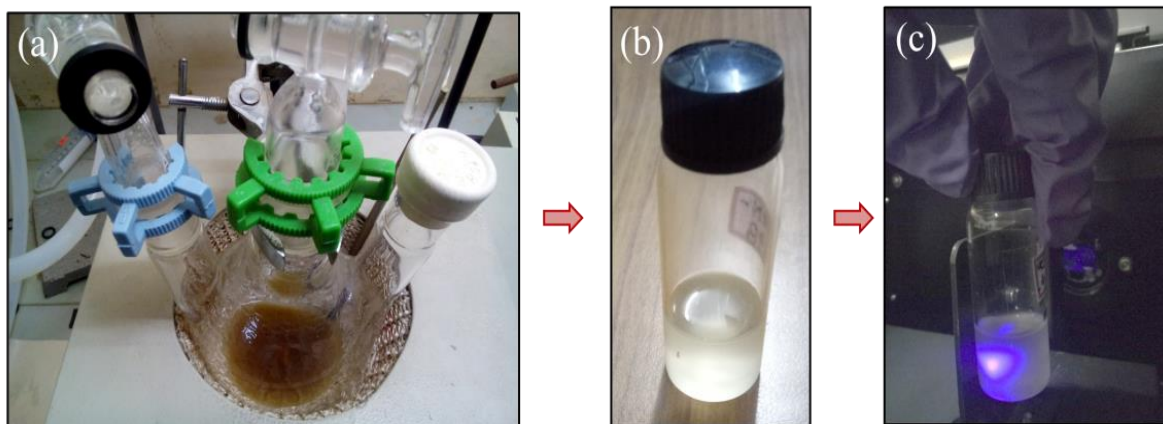
**Figure 3.3.4: (a) Upconversion emission spectrum examined with UCN-Ds colloidal solution (b) corresponding energy diagram, under 980nm NIR-laser excitation source**



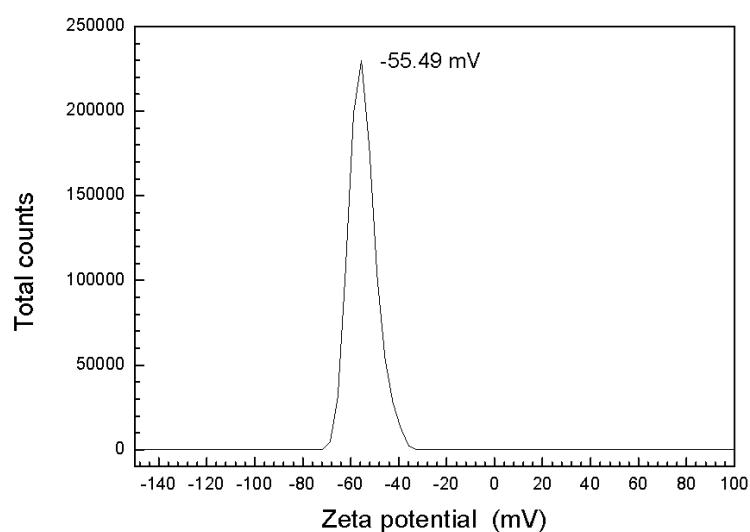
**Figure 3.3.5: (a) Upconversion emission spectrum obtained with  $\lambda_{\text{excitation}}$  of 200 nm CW laser source. In-set of (a) is showing the blue emission from UCN-ds and (b) is the corresponding energy band diagram**

It is very interesting to mention that 980nm NIR excitation resulted weak blue emissive band (figure 3.3.4) but when we examined the sample with lower excitation wavelength source as example,  $\lambda = 200\text{ nm}$ , then a high intense blue emissions occurred at 450 nm corresponds to the energy transition path,  $2H_{9/2} \rightarrow 4I_{15/2}$ . Figure 3.3.5a represents the emission spectra with their corresponding energy transitions under 200 nm excitation sources and Figure 3.3.5b represents the respective energy level diagram supported by a direct energy transfer from  $Yb^{3+}$  to  $Er^{3+}$  ion.

The insets in figure 3.3.5a shows the visible blue emissions of UCN-Ds from the UCN-Ds sample kept in glass bottle and quartz cuvette, with direct irradiation of 200nm wavelength source. Figures 3.3.6a, 3.3.6b show the UCN-Ds solution (during synthesis) in stirring condition within reaction chamber and glass bottle and 4c shows blue emissions for the UCN-Ds just after washing, respectively. These UCN-Ds are stable at least for one year owing to their high surface zeta potential value ( $\xi$ ) of about -55.49mV (figure 3.3.7).



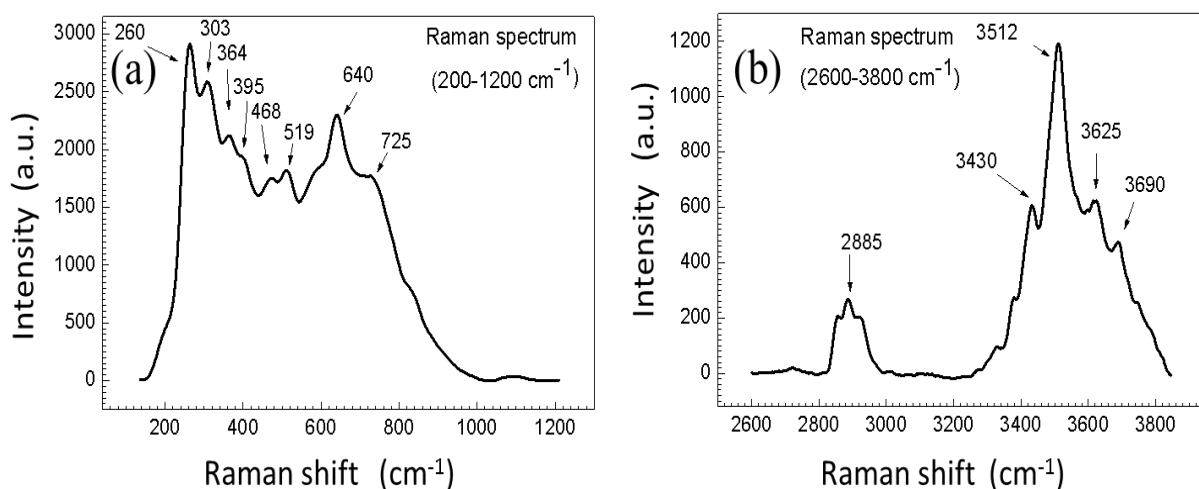
**Figure 3.3.6: (a) Image is captured during synthesis (stirring condition) of UCN-Ds at high reaction temperature( $\sim 330^{\circ}\text{C}$  -  $340^{\circ}\text{C}$ ) with 1 hr 53 mins reaction time (b) UCN-Ds colloidal sample and (c) Intense blue emission in sample glass bottle, after washing done completely**



**Figure 3.3.7: Zeta potential value found to be -55.49 mV for colloidal aqua solution of UCN-Ds**

Figure 3.3.8 shows the Raman spectrum for UCN-Ds, where the bands appeared at  $260\text{cm}^{-1}$ ,  $303\text{cm}^{-1}$ ,  $364\text{cm}^{-1}$  and  $395\text{cm}^{-1}$  (below  $700\text{cm}^{-1}$ ) confirm the formation of

hexagonal-phases [271], [312] Beyond  $700\text{cm}^{-1}$ , the appearance of strong bands at  $725\text{cm}^{-1}$ ,  $2887\text{cm}^{-1}$  and  $3512\text{cm}^{-1}$  are evidences for the presence of cubic-phases conjugated with oleic acid (capping agent). Thus, both the results obtained from XRD and Raman confirmed the formation of UCN-Ds with major  $\beta$ -phase along with a less extent of  $\alpha$ -phase.

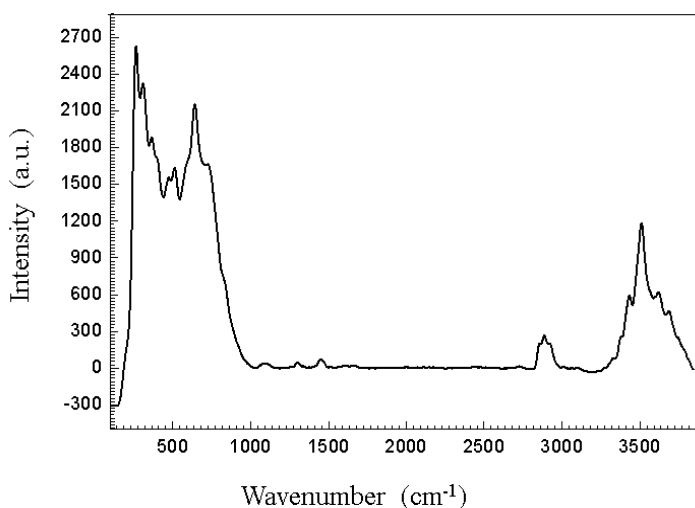


**Figure 3.3.8: (a) Raman spectrum between 200-1200nm, (b) Raman spectrum between 2600-3800nm, confirm the presence of both cubic ( $\alpha$ ) and beta ( $\beta$ ) phases in sample. The measurement was recorded at room temperature (figure 3.3.9)**

As reported earlier, the appearance of bands due to the presence of vibrational modes above  $700\text{cm}^{-1}$  are found very weak for the minute quantity of hexagonal crystalline phase in UCNPs. With the formation of  $\alpha\text{-NaYF}_4$  phase, the Raman-spectra broadened within  $1384\text{cm}^{-1}$ - $1416\text{cm}^{-1}$  and  $1041\text{cm}^{-1}$ - $932\text{cm}^{-1}$  along with two additional bands appeared in between  $703\text{cm}^{-1}$ - $687\text{cm}^{-1}$  and  $279\text{cm}^{-1}$ - $260\text{cm}^{-1}$  [313], [273]. Relatively, weaker bands appeared between  $700\text{cm}^{-1}$ - $1700\text{cm}^{-1}$  and between  $2820\text{cm}^{-1}$ - $2980\text{cm}^{-1}$  due to the presence of capping agent (Oleic Acid) [272]. Weakly intense Raman bands appeared between  $1073\text{cm}^{-1}$  and  $1445\text{cm}^{-1}$  confirm the presence of asymmetry C-O-C

and CH<sub>3</sub> stretching, respectively, whereas presence of C-CH<sub>3</sub>/C-H/O-H bonds are confirmed by the medium intense bands appeared near 2885 cm<sup>-1</sup> and 3620 cm<sup>-1</sup>.

It is also noticed that the, bands appeared between 3300cm<sup>-1</sup>-3500 cm<sup>-1</sup> are ascribed to the (-N-H) vibration band which contributes for the formations of self-assembled dendritic net- work structures between UCNPs(full range Raman spectrum has provided in figure 3.3.9).

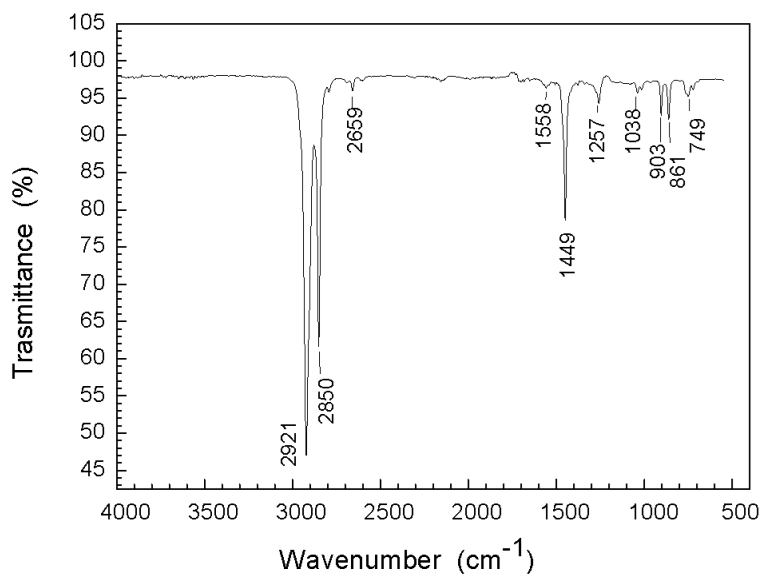


**Figure 3.3.9: Raman spectrum of UCN-Ds with entire region**

Further, the FTIR spectrum of UCN-Ds is shown in figure 3.3.10 which confirms the presence of various functional groups including N-H bending vibration at 1558cm<sup>-1</sup> and other oleic acid-capped groups at 2921cm<sup>-1</sup>, 2850cm<sup>-1</sup> appearing with highest intensity attached with the UCN-Ds.[314], [315].

However, the present analysis gives us a clear indication of  $\alpha$ - and  $\beta$ -phase formation within UCN-Ds crystals and is further supported by the TEM and XRD results (figure 3.3.1f and figure 3.3.2). The presence of two phases effectively influences for the

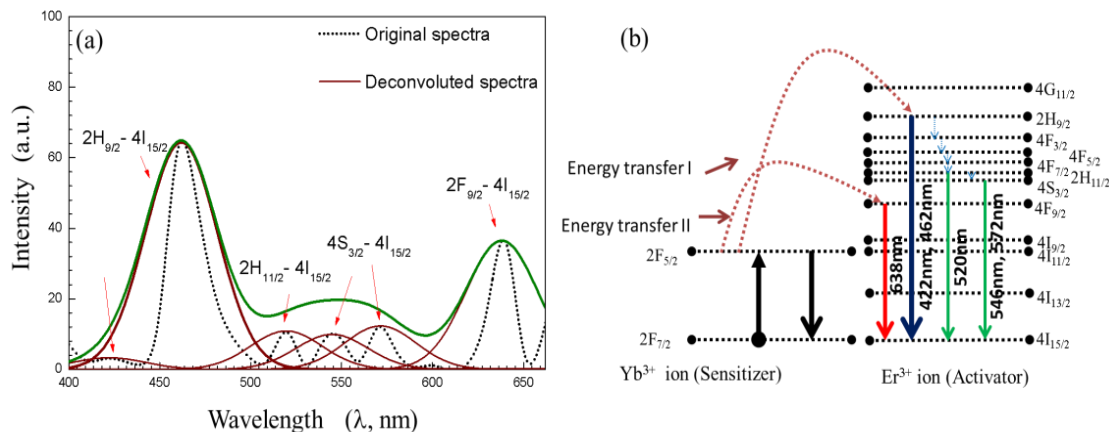
enhancement of upconversion efficiency which has been discussed in the subsequent sections.



**Figure 3.3.10: FTIR spectrum of UCN-Ds confirming the presence of different groups in oleic acid and formation of UCNPs**

PL of the UCN-Ds has also been studied. From PL study (figure 3.3.11), a visible-visible upconversion emission band is observed. The excitation wavelength source was used with  $\lambda = 450\text{nm}$  and the observed emissions obtained here are in between  $400\text{nm}$ - $650\text{nm}$ . This is an interesting observation for UCN Ds, which has never been reported even for any type of UCNPs. It can be noted that for all rare earth materials and for UCNPs only NIR to visible upconversion was reported [316],[317].

In another study, NIR-NIR upconversion was also reported previously in literature [150], [274], [311], [318], [319]. However, visible to visible upconversion is a unique phenomenon observed for UCN-Ds, and to the best of our knowledge it has never been reported.



**Figure 3.3.11: (a) Photoluminescence (PL) spectra of colloidal UCN-Ds sample obtained with 450 nm excitation wavelength (b) Energy diagram drawn from PL emission spectra in (a)**

For UCN-Ds, the observed emission bands with their highest band positions appeared at 422nm, 462nm, 520nm/546nm, 572nm and 638nm correspond to the energy transfers as,  $2H_{9/2} \rightarrow 4I_{15/2}$  and  $2H_{11/2}/4S_{3/2} \rightarrow 4I_{15/2}$  and  $4F_{9/2} \rightarrow 4I_{15/2}$ , respectively. The energy level diagram corresponds to the PL spectra (figure 3.3.11a) is shown in figure 3.3.11b. The band energy diagram includes two incidences of direct energy transfers between two rare earth ions ( $Yb^{3+}$  and  $Er^{3+}$ ) and passes through several cross relaxations and radiative and non-radiative decays that resulted in a number of emission bands. They are as follows:

Energy transfer-I occurred for  $2F_{5/2} \rightarrow 2H_{9/2}$  transition, energy transfer-II occurs from  $2F_{5/2} \rightarrow 4F_{9/2}$  resulting efficient blue and red emissions with  $2H_{9/2} \rightarrow 4I_{15/2}$  and  $4F_{9/2} \rightarrow 4I_{15/2}$  transitions, respectively. Whereas, the green emissions occurred with four non-radiative relaxations such as,  $2H_{9/2} \rightarrow 4F_{3/2}$ ,  $4F_{3/2} \rightarrow 4F_{5/2}$ ,  $4F_{5/2} \rightarrow 4F_{7/2}$ ,  $4F_{7/2} \rightarrow 2H_{11/2}$  or  $4S_{3/2}$  from  $2H_{9/2}$  level with  $2H_{11/2}/4S_{3/2} \rightarrow 4I_{15/2}$  transitions (figure 3.3.11b)

### 3.3.3 Study of Upconversion luminescence with Femtosecond (Fs)- laser source with different excitation wavelengths.

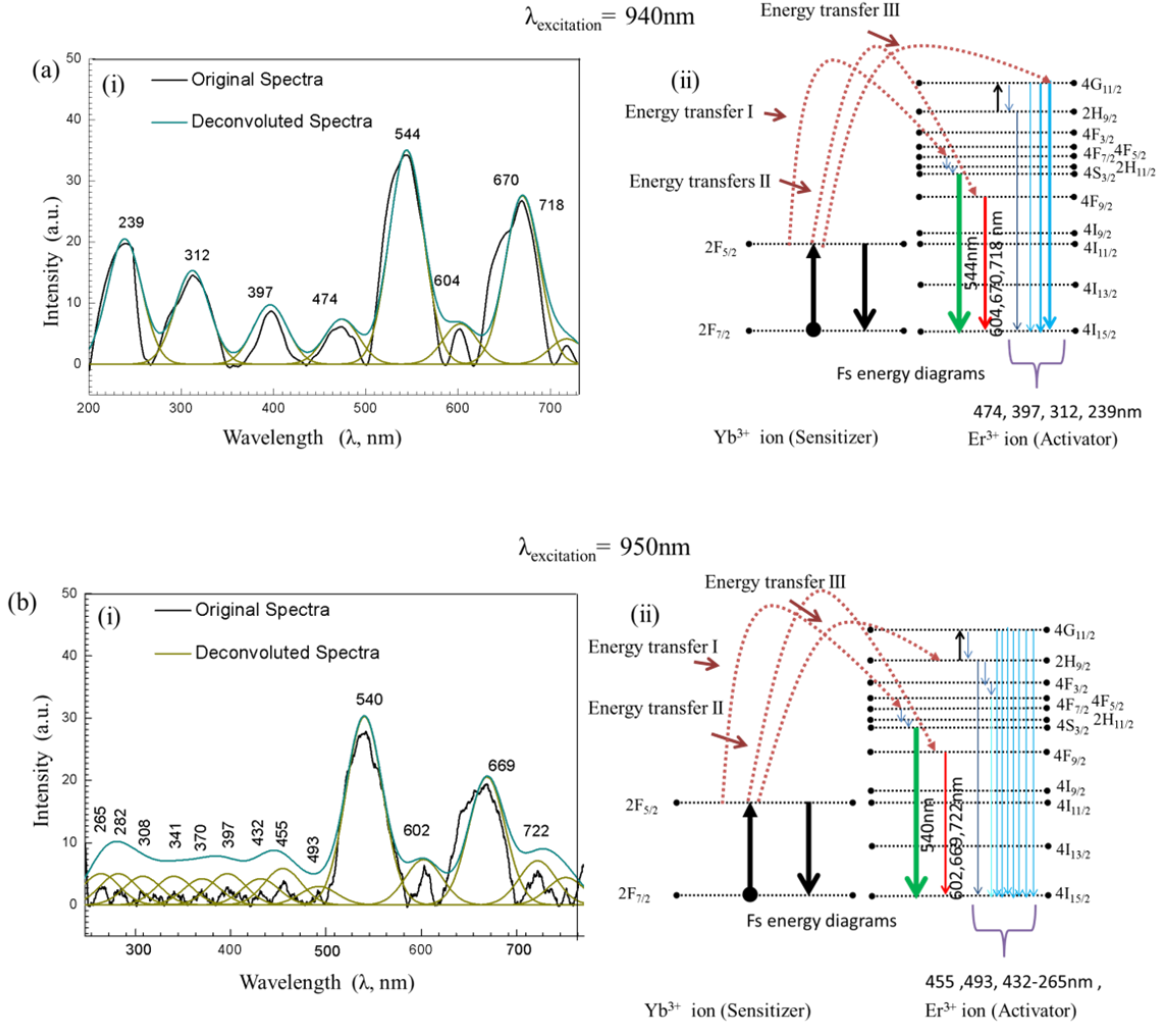
Interaction of UCN-Ds with Femtosecond-laser (Fs) results in high energy upconversion emissions under five different excitation wavelengths, such as  $\lambda = 940\text{nm}$ ,  $950\text{nm}$ ,  $960\text{nm}$ ,  $970\text{nm}$  and  $980\text{nm}$ . Each of the incident pump wavelength has yielded distinct emissions in both UV and visible regions. The emission spectra along with their corresponding energy level diagrams are shown in figure 3.3.12 and figure 3.3.13. In energy diagrams, width of each emission band is adjusted according to the intensity of the band received from the emission spectra.

#### 3.3.3.1 Fs-laser 940 nm incident pump wavelength:

Emissive bands are observed between  $239\text{nm}$ - $397\text{nm}$  in UV/violet region;  $474\text{nm}$  (blue emission);  $544\text{nm}$  (green emission);  $604\text{nm}$ ,  $670\text{nm}$  and  $718\text{nm}$  (red emission bands) in visible region (figure 3.3.12a-i). The energy level diagram with respect to the observed emission wavelengths has been drawn and shown in figure 3.3.12a-ii which states three direct energy transfers from sensitizer ( $2F_{5/2}$ ) to activator ion ( $4F_{7/2}$  and  $4F_{9/2}$ ) and thereafter it passes through the different transitions within electronic states of  $\text{Er}^{3+}$  ion. Three major energy transfer occurred and can be represented as, i)  $2F_{5/2}(\text{Yb}^{3+}) \rightarrow 4F_{7/2}(\text{Er}^{3+})$ ; ii)  $2F_{5/2}(\text{Yb}^{3+}) \rightarrow 4F_{9/2}(\text{Er}^{3+})$  and iii)  $2F_{5/2}(\text{Yb}^{3+}) \rightarrow 4G_{11/2}(\text{Er}^{3+})$ , with a total of three non-radiative relaxations such as,  $4G_{11/2}(\text{Er}^{3+}) \rightarrow 2H_{9/2}(\text{Er}^{3+})$ ,  $4F_{7/2}(\text{Er}^{3+}) \rightarrow 2H_{11/2}(\text{Er}^{3+})$ ,  $2H_{11/2}(\text{Er}^{3+}) \rightarrow 4S_{3/2}(\text{Er}^{3+})$ , respectively.

#### 3.3.3.2 Fs-laser 950 nm incident pump wavelength:

During the interaction of UCN-Ds and Fs-laser  $950\text{ nm}$  excitation source, emissive bands are obtained in between  $265\text{nm}$ -  $432\text{nm}$  of UV/violet regions;  $455\text{nm}$  (blue



**Figure 3.3.12: Upconversion luminescence spectra and their corresponding energy diagram with femtosecond (Fs) arrangement. (a) Spectra(i) and energy level diagram(ii) under 940nm; (b) spectra (i) and energy level diagram(ii) under 950nm; excitation wavelengths**

emission); 493nm (intermediate region); 540nm (green emission); 602nm, 669nm and 722nm (red emissions) in visible regions (figure 3.3.12b-i). Intensities of bands in lower wavelengths (265nm-493nm) appeared to be weak compared to the green and red emissions but definitely with few numbers. The energy level diagram is shown in

figure 3.3.12b-ii three direct energy transfers and following energy transitions, i)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+})$ ; ii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{9/2}(Er^{3+})$  and iii)  $2F_{5/2}(Yb^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ , with a total of five non-radiative relaxations,  $4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ ,  $2H_{9/2}(Er^{3+}) \rightarrow 4F_{3/2}(Er^{3+})$ ,  $4F_{3/2}(Er^{3+}) \rightarrow 4F_{5/2}(Er^{3+})$ ,  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}(Er^{3+})$ ,  $2H_{11/2}(Er^{3+}) \rightarrow 4S_{3/2}(Er^{3+})$ .

### 3.3.3.3 Fs-laser 960 nm incident pump wavelength:

Once UCN-Ds was interacted with Fs-laser (960 nm), emissive bands obtained between 282nm-400nm in UV/violet region; 465nm (blue emission); 545nm (green emission); 604nm, 669nm and 721nm (red emissions) in visible regions (figure 3.3.13a-i). Intensities of bands in lower wavelengths (282nm-465nm) are appeared to be weak compared to the green and red emissions. Green and red emissions obtained in the same intensity.

The corresponding energy level diagram is shown in figure 3.3.13a-ii with three direct energy transfers, such as i)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+})$ ; ii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{9/2}(Er^{3+})$  and iii)  $2F_{5/2}(Yb^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ , similar to 950nm, differing only with number of non-radiative relaxations following the energy transfer path,  $4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ ,  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}(Er^{3+})$ , and  $2H_{11/2}(Er^{3+}) \rightarrow 4S_{3/2}(Er^{3+})$ .

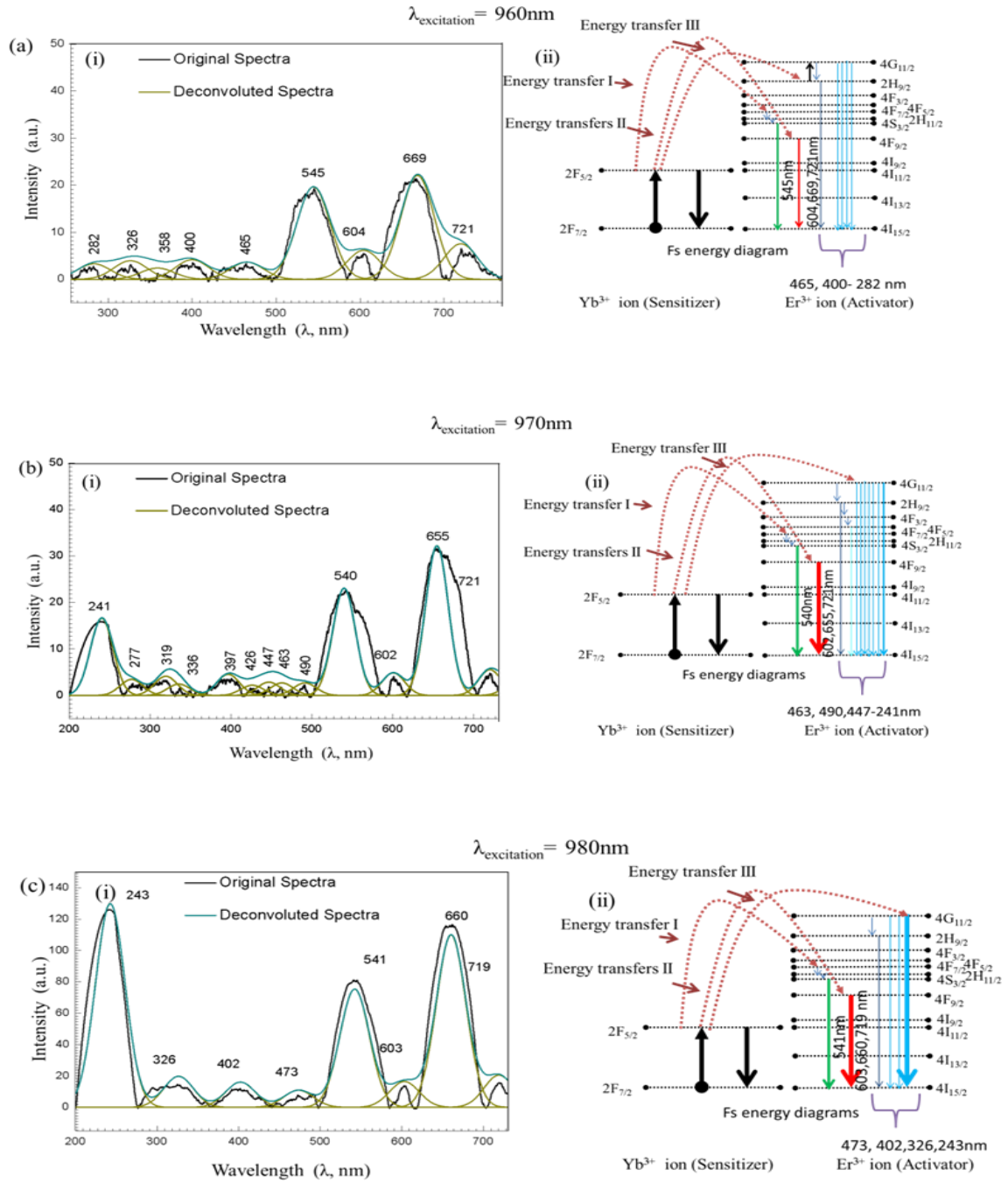
### 3.3.3.4 Fs-laser 970 nm incident pump wavelength:

UCN-Ds were also interacted with Fs-laser with 970 nm irradiation and emissive bands obtained in between 241nm-447nm in UV/violet regions; 463nm (blue emission); 490nm (intermediate region); 540nm (green emission); 602nm, 655nm and 721nm (red emissions) in visible regions (figure 3.3.13b-i). Emission bands appeared in lower wavelengths (241nm-490nm) are quite strong in intensity; even one high intensity band is appeared with 241nm peak position in UV region. These emission bands can be explained with separate energy band diagram in figure 3.3.13b-ii. Emission occurred due to three direct energy transfers

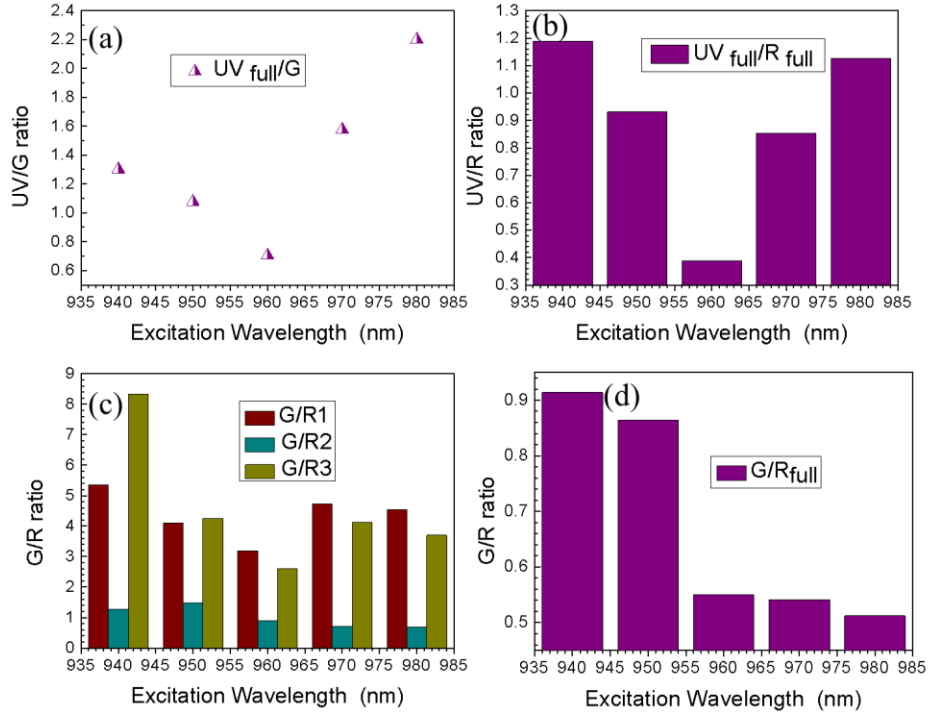
between the different energy levels, such as i)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+})$ ; ii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{9/2}(Er^{3+})$  and iii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4G_{11/2}(Er^{3+})$ , including five non-radiative relaxations,  $4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ ,  $2H_{9/2}(Er^{3+}) \rightarrow 4F_{3/2}(Er^{3+})$ ,  $4F_{3/2}(Er^{3+}) \rightarrow 4F_{5/2}(Er^{3+})$ ,  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}(Er^{3+})$  and  $2H_{11/2}(Er^{3+}) \rightarrow 4S_{3/2}(Er^{3+})$ .

### 3.3.3.5 Fs-laser 980 nm incident pump wavelength:

Finally, to compare the upconversion of UCN-Ds obtained after interaction with CW-980 nm NIR, the same sample interacted with the Fs-laser with  $\lambda = 980$  nm. Once interacted with Fs-laser the upconversion emissive bands are observed between 243nm-402nm (in UV/violet regions); 473nm (blue emission); 541nm (green emission); 603nm, 660nm and 719nm (red emissions) in visible regions (figure 3.3.13c-i). A very high intensity band is observed in UV region compared to others. The energy level diagram is shown in figure 3.3.13c-ii with three direct energy transfers such as, i)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{7/2}(Er^{3+})$ ; ii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4F_{9/2}(Er^{3+})$  and iii)  $2F_{5/2}(Yb^{3+}) \rightarrow 4G_{11/2}(Er^{3+})$ , with three non-radiative relaxations, (i)  $4G_{11/2}(Er^{3+}) \rightarrow 2H_{9/2}(Er^{3+})$ , (ii)  $4F_{7/2}(Er^{3+}) \rightarrow 2H_{11/2}(Er^{3+})$  and (iii)  $2H_{11/2}(Er^{3+}) \rightarrow 4S_{3/2}(Er^{3+})$ . Thus, five emission spectra in figures 3.3.12 and 3.3.13 revealed the high-energy emissions under different excitation wavelengths, which never been observed for CW-NIR laser (980 nm). Among five of them, the highest UV emission (UV<sub>full</sub>) was found under 980nm excitation wavelength. Apart from that, the other emissions green (G)/red(R) are also significant and appear with highest intensity in case of 980nm excitation wavelength. Blue emissions are also observed in each of the cases.



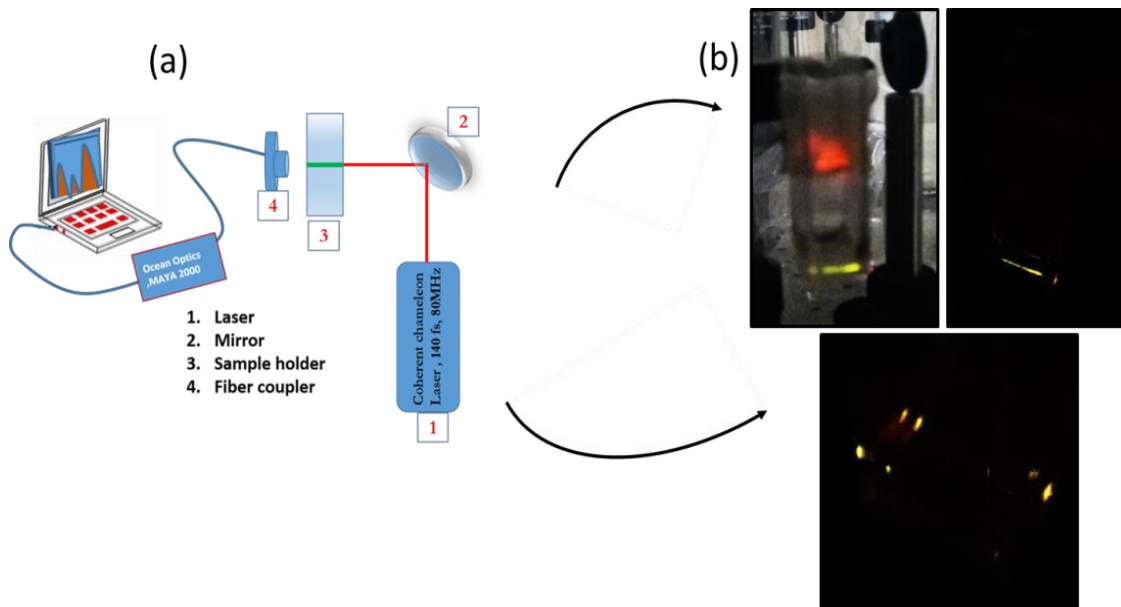
**Figure 3.3.13: Upconversion luminescence spectra and their corresponding energy diagram with femtosecond (Fs) arrangement. (a) spectra(i) and energy band diagram(ii) under 960nm; (b) spectra(i) and energy level diagram(ii) under 970nm; (c) spectra(i) and diagram(ii) under 980nm excitation wavelengths**



**Figure 3.3.14: Shows the ratio plots for the intensity of different emission: (a) UV<sub>full</sub>/G, (b) UV<sub>full</sub>/R<sub>full</sub>; (c) G/R1, G/R2, G/R3; (d) G/R<sub>full</sub> vs excitation wavelengths**

Furthermore, intensity ratios between UV, R and G under Fs-laser treatment were calculated for five different excitation wavelengths and are shown in figure 3.3.14. Intensity changes for different emissions (UV, G and R) under different excitation wavelengths (940nm, 950nm, 960nm, 970nm and 980nm) resulted in different relative ratio plots UV<sub>full</sub>/G; UV<sub>full</sub>/R<sub>full</sub>; G/R1, G/R2, G/R3; and G/R<sub>full</sub> shown in figure 3.3.14a, figure 3.3.14b, figure 3.3.14c, and figure 3.3.14d, respectively. Different in efficient population of photons in different energy levels under 940nm-980nm excitation sources could be the possible reasons for the occurrence of different intensity.

The experimental set-up of Fs-laser has provided in figure 3.3.15.



**Figure 3.3.15: (a) Schematic of Femtosecond laser (Fs) set-up arrangement (b) Images are captured while visible emissions are observed in cuvette-sample once it is excited with Fs-laser sources**

### 3.3.4 Discussion:

It can be noted that upconversion luminescence properties with Fs-laser irradiation for different rare earth elements along with their applications were reported elsewhere [90], [320]–[327]. Such as YVO<sub>4</sub> single crystal upconversion luminescence was observed under infrared (IR) Fs-irradiation which resulted in broad characteristic emission in visible region (350nm-600nm) [320]. For, Ce<sup>+3</sup> doped YAP crystal, upconversion luminescence appeared in both ultraviolet and visible region under a focused 800nm Fs-laser irradiation [321]. Visible emission bands were also found with NaYF<sub>4</sub>-glass ceramic doped with Er<sup>3+</sup> ions under 800nm CW laser treatment [322].

Intracellular imaging of cancer cells (such as HeLa cells, cervical cancer cells, collected on 8 Feb, 1951 from Henrietta Lacks), by using the Fs-pulse laser (100Fs, 920nm) was performed with very high resolution using non-functionalized NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup>. [323] Further, red and green upconversion luminescence was reported with 5% Er<sup>3+</sup> doped NaYF<sub>4</sub> nanocrystals with using two Fs-laser (excitation wavelengths 800nm, 1490nm) simultaneously. [325] Tunable enhanced ultraviolet luminescence can be developed by using UCNPs for recording highly effective and rapid in situ-real time biocompatible photoactivation [324]. Optogenetic proteins have huge applications in neurology and brain science along with cell biology. However, it was found that the narrow excitation wavelength limits the applications of optogenetics which has recently manipulated and improved using tunable Fs-laser system [328]. Moreover, for ultra-deep in-vivo bio-imaging non-linear optical effects using Fs-laser excitation in AIEgen nanocrystals was found effective [329]. By a group of researchers, it is reported that Ti:Sapphire Fs-laser, with pulse duration of about 160 Fs, is very useful for generation of high harmonic as example fifth harmonic generation from photonic crystal and is useful in designing opto-electronic devices with effectively high efficiency [327]. Further, it can be noted that for the rare-earth doped luminescent nanomaterials, colour tuning is having important significance for several applications such as designing of display device, bio-labelling, optoelectronic device etc. The tuned luminescence properties can be developed from Er<sup>3+</sup> doped glass ceramic using 800 nm Fs-laser excitation sources [330]. Thus, the present findings i.e., the development of UCN-Ds and their improved luminescence properties in UV and visible ranges are very interesting and can be used in device making for industrial (optoelectronics) to biomedical such as for disease diagnosis and therapeutic applications by targeting the infected cells with enhanced efficiency.

### 3.3.5 Summary and Conclusions of PART III:

Dendritic polymers are known for decades, however, dendritic upconverting nanoparticles are never been reported. In this work, dendritic NaYF<sub>4</sub> nanoparticles (UCN-Ds) with lanthanides (Yb<sup>+3</sup>, Er<sup>+3</sup>) have been synthesized for the first time with one pot chemical synthesis approach, by controlling the reaction temperature in in-situ condition, without adding any external dendritic polymers during synthesis process. UCN-Ds contain both of the  $\alpha$ - and  $\beta$ -phase within its solid structure and are very stable. Presence of these two phases in dendritic UCNPs could be the cause of high energy upconversion and make them very seminal and are with caterpillar/necklace type of structure.

This self-assembled structural dendritic-network may be allowed for designing 2D nanostructures with defining clear geometry.

Apart from that, the bright blue emission make them very attractive with lower excitation wavelength source with visible to visible upconversion [297], [331]. With higher wavelength source with Fs-laser, UV emission becomes prominent making them a suitable candidate for industrial and biomedical applications [332], [333], [334]. The different emissions (green/red /blue/cyan/UV) could be useful in colour tuning and magnetic sorting [335], [336] by changing their excitation wavelengths.

## **Chapter 3 RESULT AND DISCUSSION**

# **PART-IV**

**3.4 (Part-IV): Morphologically controlled upconverting self-assembled superlattices (SAM-SL UCNPs) prepared by one-pot chemical approach: Efficient luminescence observed under different pump powers**

**Outcome:** Manuscript is under preparation

### 3.4.1 Introduction:

Since the very early age, the design of aligned, self-assembled nanoparticles is having great importance for its uses in various fields including electronic device fabrication to the biomedical applications [1]. Self-assembled materials are available in nature. However, it can also be designed artificially by changing the different interactions between the nanoparticles and through varying the kinetic or the thermodynamic parameters in-situ. Biomaterials possess intrinsic behaviour and comprise self-assembled structures similar to the naturally occurring ones [2]. However, self-assembled structure formation induced by several factors and the mechanism of the formation fundamentally needs to be understood essentially to fine tune its properties [3]–[5]. Nanoparticle superlattice is one of the well-defined self-assembly of highly ordered nanoparticles and is different from material of its bulk phase crystal, isolated nanocrystal and even disordered nanocrystal assemblies, which exhibits different enhanced properties e.g., conductivity, mechanical properties, optical properties, plasmonic properties, etc. depending on its order of packing/arrangement compared to its bulk[6]–[10]. Nanoparticle superlattice can be constituted through the bottom-up self-assembly approach where the process either can be in equilibrium or in a non-equilibrium state. Usually, to achieve the high-quality order of nanoparticles in superlattices, the process involves soft ligands or capping agents which further help to tune/programme the artificial structure and its properties through functionalizing the nanoparticles and by changing the particle-particles binding interactions. These soft ligands further specially control the nearest-neighbour spacing, lattice structure and superlattice properties [6]. Thus, the collective interactions between organized superlattice nanoparticles in both of two dimension (2D) as well as three-dimension (3D) make them effective for usage in electronic and optical devices[11]–[20]. It can be noted that the formation of superlattices in large nanoscale area with synthesizing vastly the monodisperse nanoparticles is critical.

In 1994, Janos Fendler was first introduced the concept of superlattice of nanoparticles [21], [22] and constitute CdS nanoparticle (dia~ 26.5 Å to 34.0 Å) superlattice [21] *which was prepared* at the air-water interface in a Langmuir film balance and observed the change in fluorescent properties. In the same year using the similar method, at air-water interface in a Langmuir film balance they constitute superlattice *of Ag nanoparticle (dia.~100 Å)* (multilayer) and observed the change in the optical and eletrooptical properties [22]. In subsequent year 3D quantum dots (QDs) (CdSe, 20Å) superlattice structure (5µm to 50 µm) was made by Murray et al. where the spacing between the dots were controlled within near atomic scale precision [23]. They observed the discreet and size dependent optical absorption and band edge emission due to the quantized electronic transition of the individual QDs. Comparison to the optical properties between colloidal QDs and closed packed superlattice structure, the band spectra were identical, however, the shape of the emission spectra of the QDs in the superlattice was reformed and red-shifting due to the inter-dots coupling was observed [23]. Superlattices of cobalt nanocrystal prepared from solution phase dispersion of Co nanoparticle in octane with oleic acid capping agent with nanocrystal spacing of ~ 4 nm were prepared which exhibited spin-dependent electron tunnelling [24]. In the similar line, nanoparticle superlattice alter the materials properties from its bulk, such as insulator-to-metal transition[25], leads to the enhancement of p-type conductivity (e.g., PbTe/Ag<sub>2</sub>Te) [8], high order vibrational coherency (e.g, FCC Ag NPs, plasmonic properties [7] *etc.* with retaining their basic crystal structure [6].

In this chapter, the synthesis of upconversion nanoparticles-superlattices (UCN-SL) in many defined and order structures are reported. Self-assembled UCN-SL are prepared herein by one pot chemical synthesis approach and their upconversion and fluorescent properties have been studied through continuous wave laser (CW-Laser) as well as with femtosecond laser (fs) irradiation.

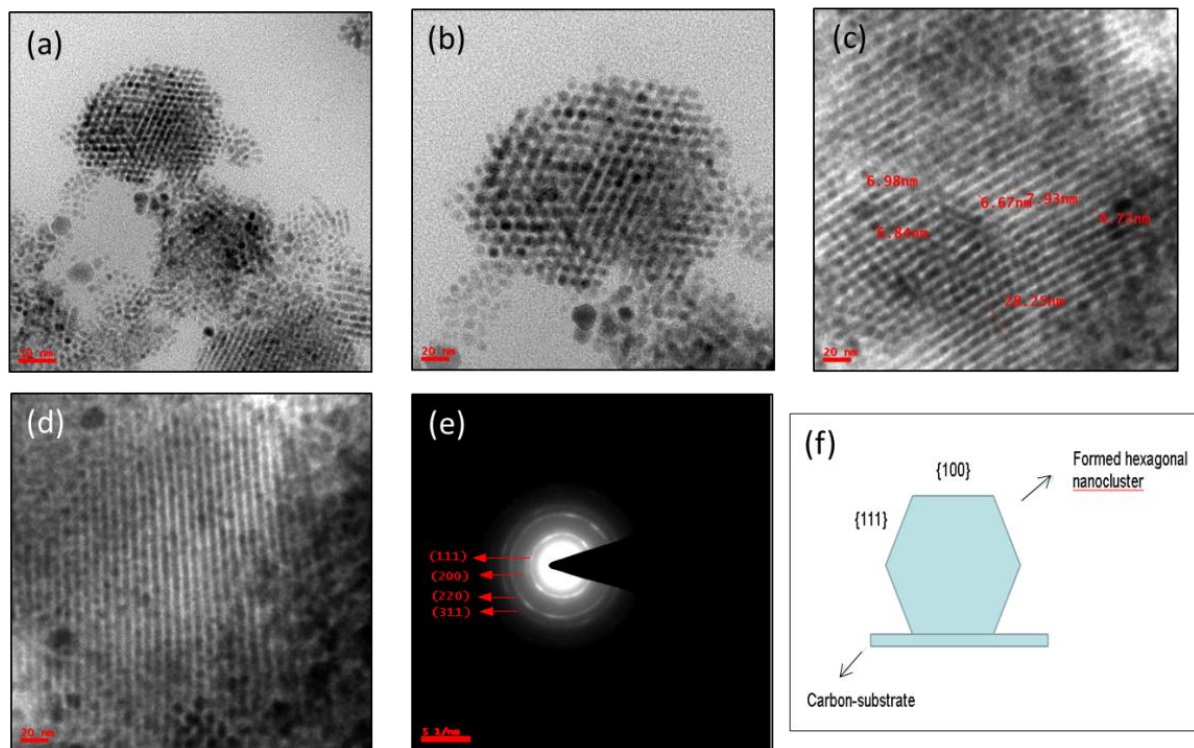
It can be noted that, a huge number of potential applications of UCNPs make them significant in research due to their unique fluorescence and luminescence properties[26]–[30]. For the first time this work reports on the controlled synthesis for achieving shape and size directed UCN-SL having efficient fluorescence and luminescence properties under continuous wavelength (CW)source as well as femtosecond-laser (fs) source.

Further upconversion emissions at ultraviolet and visible emissions have been investigated. The synthesis procedure applied here to form UCN-SL is a modified approach of the synthesis method developed by our group previously. The entire reaction process was carried out in an inert gas (Argon) atmosphere. The different self-assembly superlattice structure have been formed in in-situ with varying the condition. Usually researchers design this type of assembled structure in at-least 2<sup>nd</sup> stage of the whole synthesis procedure [1], [3]–[5]. However, we are able to prepare such assembled structure in one-pot chemical synthesis approach. The beauty of the process is that the entire synthesis process consumes less time to obtain the self-assembled UCN-SL structures. Further, how the UCN-SL with different architecture exhibited different upconversion luminescence properties also have been elucidated. As-synthesized UCN-SL structures represented here not only generate new physical properties from bulk materials but also new phenomenon for interactions between particles at nanoscale have been found out. In order to produce the particular self-assembled UCN-SL pattern in synthesized nano- material we followed few controlled reaction parameters. By applying those key factors, the correlative arrangements of nanocrystal building blocks with their sizes and the spacing between those crystals are maintained in a self-assembled long-range order. The precisely engineered nanocrystal sizes and systematic shaped assembly are treated as building blocks to generate improved ones. Additionally, for the different UCN-SLs the different in intensity of

emission and their position and shifting, internal upconversion quantum yield (Internal UCQY) and external upconversion quantum yield (External UCQY), photoluminescence behaviour, fs-laser power dependent luminescence and the number of absorbed photons taken part in the process ( $n$ , where ‘ $n$ ’ is the number of absorbed NIR photons per emission under fs-laser excitation power) has been calculated. The controlled morphology with efficient upconversion fluorescence and luminescence of these UCN-SL structures may discover considerable applications in different fields such as lasers[31], [32], diodes[33], [34], display-techniques and energy –related applications[30], [35]–[42].

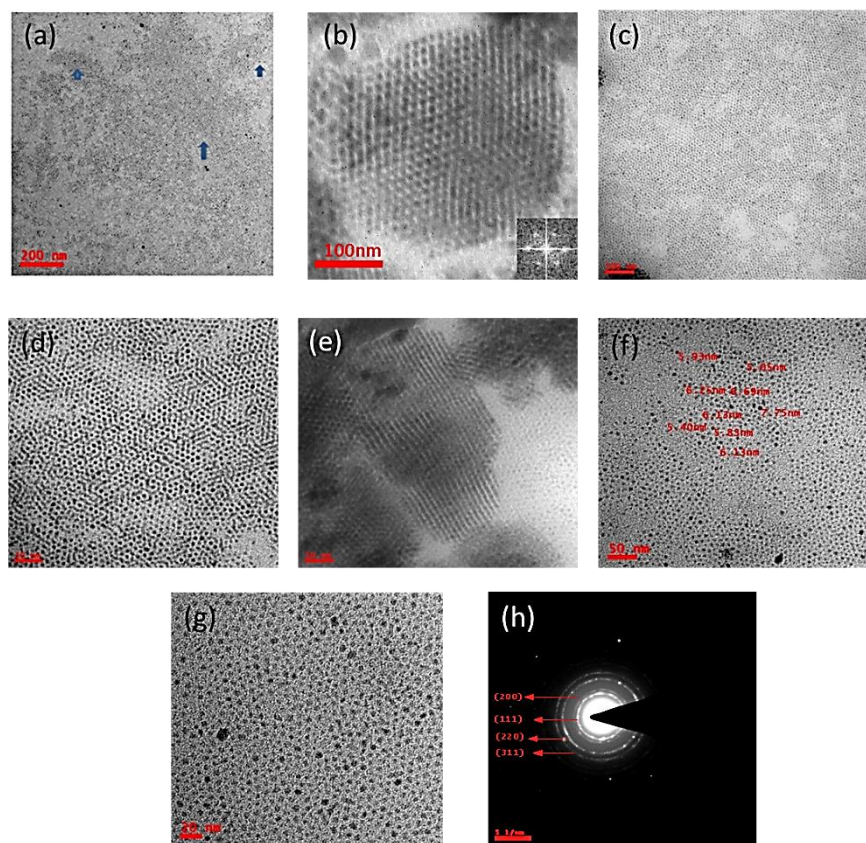
### **3.4.2 Results and Discussion:**

As-synthesized ordered self-assembled UCN-SL those nanocrystal-building blocks are obtained according to the method as discussed in the experimental section. The colloidal chemistry plays an important role to self-organize the UCNPs in super lattice array within its colloidal solution. Formations of nanoclusters also occurred in some places on the sample-grid on which the clusters are made-of few individual particles which are isolated from each other in a specific way so as to develop the periodic and parallel array. The stability of the synthesized super lattice colloidal solution proves the presence of some interaction between the particles themselves. As the nanoparticles are covered with ligands-Oleic acid, they are dispersed transparently in solvent (cyclohexane). For superlattice of nanomaterial, it is the structure of surface and crystal on which their chemical and physical properties depend.



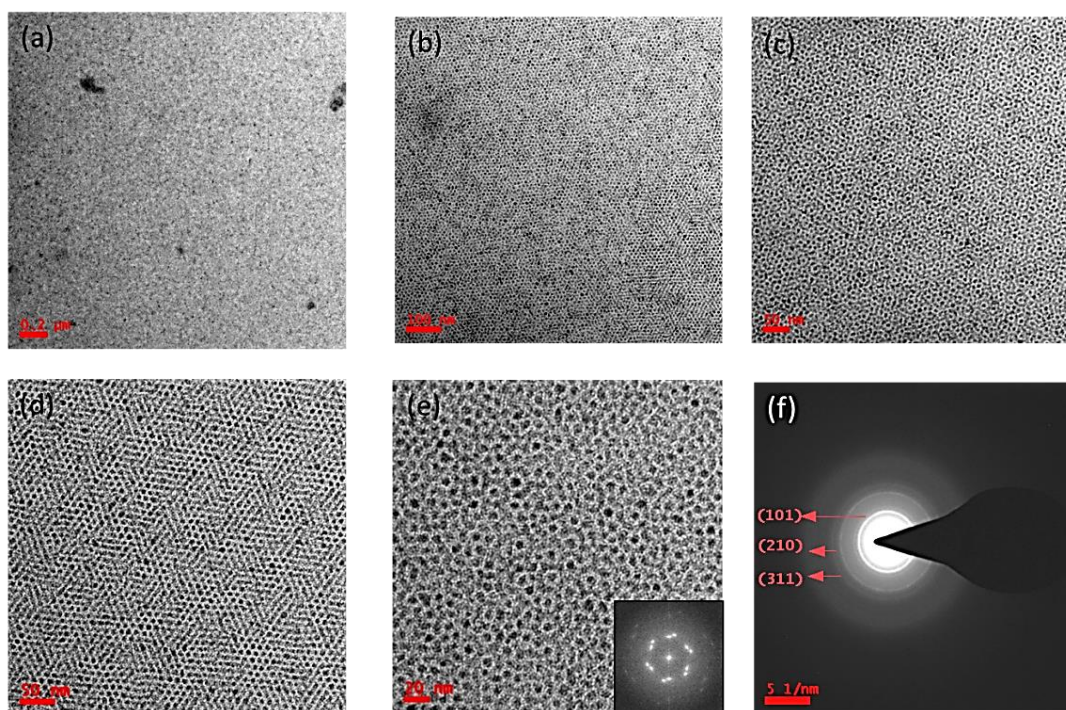
**Figure 3.4.1: TEM images of self-assembled formations of UCNPs with 15-20 mins high reaction temperature, panel (a) - 50nm scale bar, panel (b-d) - 20nm scale bar, panel (e)- SAED pattern. (b) - formation of {100} and {111} facets on substrate, (c,d) - formations of UCN-nanochips, (a) show planar defect-twinning effect, panel (f) The cross section of a formed nanocluster on substrate**

TEM micrographs (figures 3.4.1-3.4.3) revealed the structures of those size and shape controlled self-assembled nanocrystals. TEM images for different UCN-SL colloidal samples are exhibiting the morphology of self-organized and periodic nature of synthesised materials.



**Figure 3.4.2 : TEM images of self-assembled formations of UCNPs with 51 mins of high reaction temperature, panel a- 200nm, panel b, c - 100nm ,panel d-f- 50nm panel g- 20nm, panel h- SAED pattern. (a), (c), (f), (g)- Formation of monodisperse nanoparticles, (a)- Short range particle-packing order, (b) - conversion of an FFT image derived from a hexagonal cluster orientation where the synthesized nanocrystals are oriented along [100], [111] (c)-planar defect with twinning effect, (d)Hexagon arrangement and (e)rod-like parallel assembly of synthesized UCNPs.**

In self-assembled superlattices, the shape and size-controlled nanoparticles act like molecules which can be considered as building blocks to construct 2D and 3D self-assembled superlattice-clusters.



**Figure 3.4.3: panel ( a ) -200nm, panel (b)- 100nm, panel (c,d) – 50nm, panel(e)- 20nm, panel (f)- SAED pattern, (c,d,e) - clear 3D assembly with a complete hexagon-type formations**

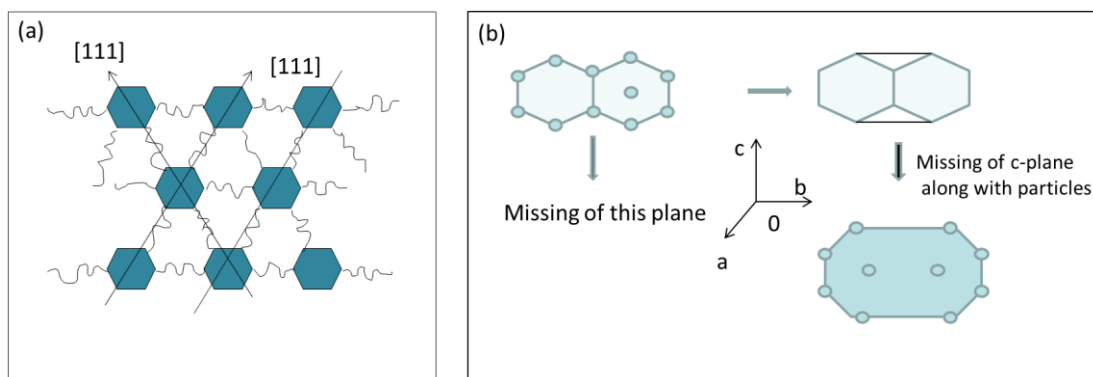
With the size uniformity and orientational order of particles in SL-structures the crystallography arrays have also been clearly identified. The long chains of organic capping agent (oleic acid) contributed as both as protectors as well as interparticle–bonding between two particles. The TEM studies reveal the formations of three different type of SL-structures obtained from differently prepared samples. Hence, the evaporation-rate of carrier solvent was also responsible to organize different-kinds of self-assembled superlattice structures.

The self-assembled superlattice formations (SAM-SL) of synthesized UCNPs prepared with different reaction conditions have been shown in figures 3.4.1, 3.4.2 and 3.4.3.

In figure 3.4.1, formations of SAM-SL UCNPs is shown with lowest reaction time (15-20 mins). For figure 3.4.2, high reaction temperature (300°C) was maintained for almost 51 mins. In figure 3.4.3, SAM-SL UCNPs were formed after 1 hr, 50 mins of high reaction temperature.

For the first experimental set-up (exset-1; maintained 15-20 mins of high reaction temperature (300°C)), TEM images (figure 3.4.1) revealed the formation of self-assembled structures having [100] and [111] orientation of the organized superlattices. Throughout the sample a number of discrete nanoclusters have been formed. The shape of each cluster is almost hexagonal which are made-up with particles arranged in regular arrays parallel with each other. On nanocluster-surface the distance between two parallel particle-lines is measured to be 5 nm which is uniform throughout the cluster. Throughout one nano-cluster the particles are monodispersely distributed with uniform sizes. This uniform size of the particles is maintained throughout the sample. In each nanocluster, the average diameter of UCNPs is between 7-8 nm. The orientation of the particles along the surfaces of the hexagonal shaped nano-cluster was confirmed by figure 3.4.1b which suggests the formation of {100} and {111} facets on substrate with having thermodynamically unstable crystal growth. The cross section of such a nanocluster-formation is given in figure 3.4.1f. Figures 3.4.1c and 3.4.1d reveal the formations of UCN-nanochips (as looks like a particular disk shape) where the UCN-particles are situated at lower levels of a disk-layer constructing mostly (111) planes along the surface of a cluster though (100) planes have also been appeared through some regions forming 3D-self-assembly.

For second set of experiment (exset-2; reaction performed for 51 mins at reaction temperature of 300°C), TEM images (figure 3.4.2) revealed very interesting results, as shown at different magnification. During experimental procedure, for a longer time materials were heated compared to the previously formed 3D- assembled nanodisk shaped (check 3D/2D-self-assembled superlattices) and unstable superlattice-arrangements are formed throughout having a different kinds of arrangement such as a monodisperse arrangement occurred (as shown in figures 3.4.2f and 3.4.2g), hexagon arrangement with situating one particle inside (figure 3.4.2d), rod-like cluster arrangement with parallel assembly (figure 3.4.2e). Monodisperse particles occupy most of the places in sample as it seems an extra heat was employed into the clusters and self-assembled structure broken into separate monodisperse particles. Hence some places throughout the sample where their arrangement is a perfect hexagon with uniform particle-sizes viewed with 50 nm magnification (see panel 2d) is traced. This phenomenon is very interesting.



**Figure 3.4.4: (a) A bundle of surfactants act as channels between the assembled nanoparticles containing different stretches and vibrations; O-H, C-O, C-C, C-H, CH<sub>3</sub> ; (b) A schematic diagram of planar defects appeared in SAM-SL UCNPs**

Thus materials were heated for further longer period of time amount of reaction temperature with corresponding reaction time was not enough to break all such

nanoclusters completely into single monodisperse particles but many parts of them were able to overcome the energy barrier and formed discrete single particles. As a result, some portions of the sample are still having cluster-formations, and some are having discrete monodisperse particles.

To analyse and review this interesting part again we increase the reaction time to almost 1hr 50 mins (third experimental set up; exset-3) at 300°C. TEM images for the sample of exset-3 are shown in figure 3.4.3 which a hexagon-shaped arrangement consisting of total of 7 particles, one particle is in middle and surrounded with six similar-sized particles. This type of arrangement was observed throughout the whole substrate are they are in a long-range-order. Further, the TEM images shown in figure 3.4.3 depicts clearly that most of the 2D-superlattices (as shown in figure 3.4.2) have been converted into a 3D-superlattice arrangement (figure 3.4.3). This beautiful 3D arrangement occurred with a number of monodisperse particles. In this arrangement, the average particle sizes varied from 5nm-9nm. Thus, from TEM images it is clear that there types of arrangements could be more useful to consider the shape-symmetry of as-synthesized nanocrystals and especially 3D objects with 2D projected image. There is one key parameter for TEM to analyse the packing between the particles; adjustable ratio between particle-size and interparticle distance in the presence of passivated surfactant (here Oleic acid acts as surfactant), whose chain length can be controlled. This key parameter is well controlled in our synthesized material (figure 3.4.4). TEM samples were prepared by placing the droplets of NaYF<sub>4</sub>:Yb<sup>3+</sup>; Er<sup>3+</sup> superlattice colloidal solution on the grids and then drying properly under ambient temperature (25°C). Though the drying time was different for different sets of three samples, but drying temperature was 25°C. An amount of 8-10 µL of concentrated colloidal solution was taken on TEM grid. Then allowed drying for 20-25 mins. Figure 3.4.2 shows 2D (2-dimensional) monolayer self-assembled superlattice-UCNPs. Particle-packing order

is observed in short-range orders as indicated by arrowheads region as it is shown in figure 3.4.2a.

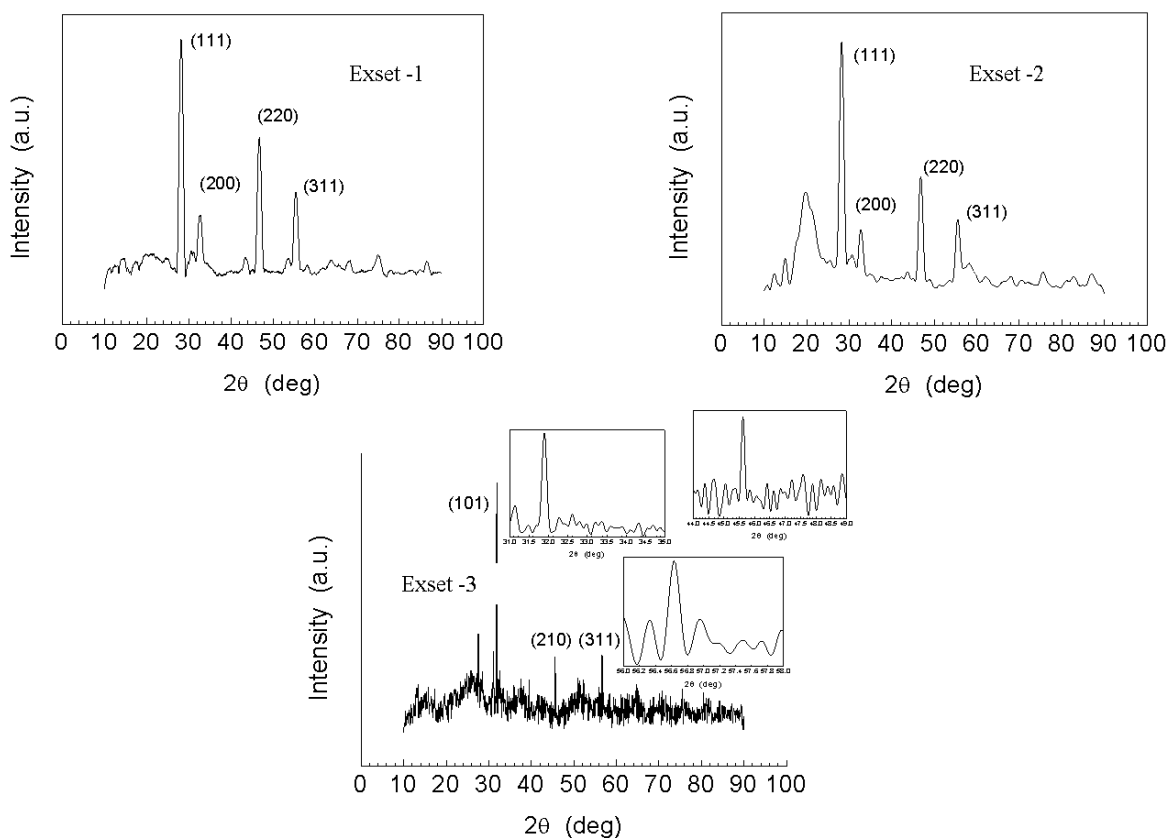
From different views of samples in the prepared grids, the TEM images have been captured for confirming the construction of 3D-SAM-SL-UCNPs models. Figures 3.4.3c and 3.4.3e show the perfect hexagon shaped arrangement with one particle at centre surrounded by six particles and exhibited six-fold symmetry.

From TEM images, for both in 1<sup>st</sup> set (figure 3.4.1) and 2<sup>nd</sup> set (figure 3.4.2), we have traced locations in short-range order arrangements, where planar defects- Twinning effect along with stacking faults have taken place between UCN-particles. In twinning defect, a plane is shared by two subgrains in such a way that one grain can be considered the mirror image of other. Though in our synthesized material this twinning effect is not that strongly observed but still their presence owes to less volume and surface energies of smaller particles introduce such planar defects in the self-assembled UCN-particles.

The other planar defect- Stacking fault has also been observed clearly in figure 3.4.2c by missing the vertical plane (say-plane-c) between two hexagon-shaped nanoparticles. The missing of two or four particles from its regularity is shown in figure 3.4.4b.

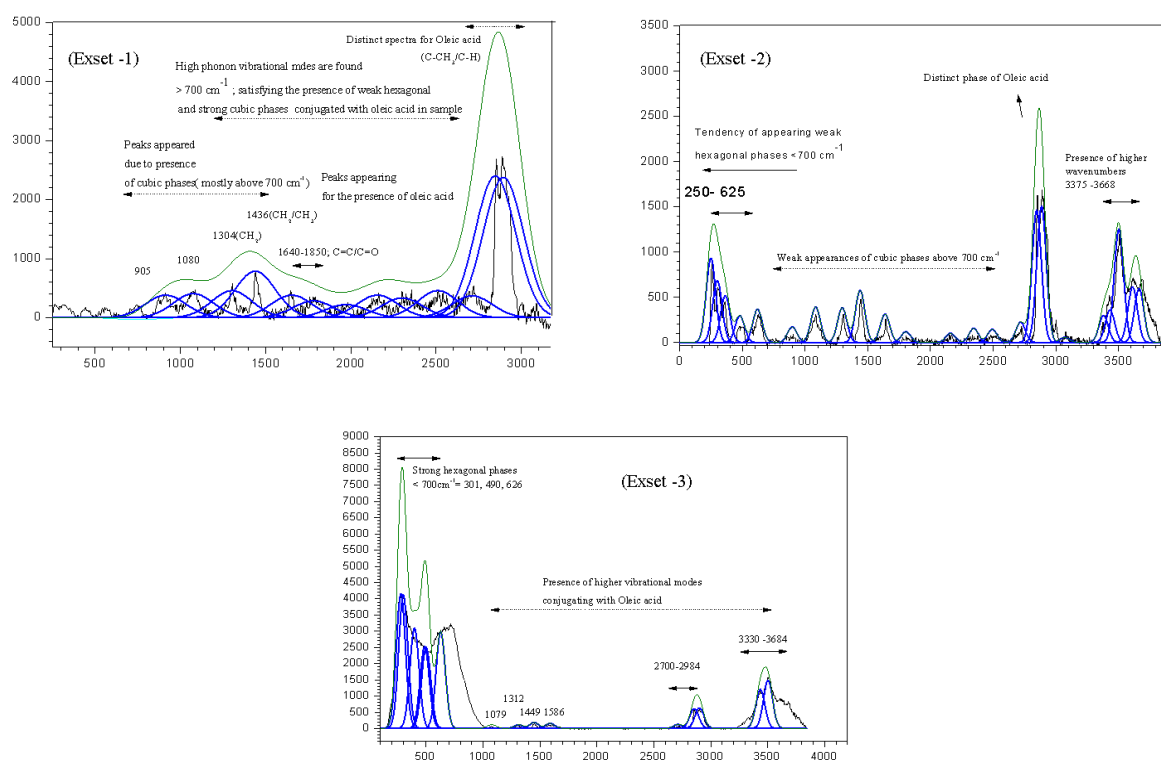
In figure 3.4.3, different magnified TEM images have been shown with the formation of completely a new kind of 3D-self-assembly in UCNPs. Figure 3.4.3 confirms the formation of close-packed monolayer having particle-sizes of diameter 6-7nm at different magnifications (scale bar 200nm, 100nm, 50nm, 20nm). Hexagonal-type arrangement has been observed in figures 3.4.3c, 3.4.3d and 3.4.3e, which provide a three-layer assembly. A 3D-assembled SL structure with multilayers is observed in

TEM image (figure 3.4.3d). Following slow evaporation of carrier solvent a 3D-SL (figure 3.4.3d) was obtained with hexagon-type arrangements sharing 12 particles with each other. Thus, figure 3.4.3 indicates that the synthesized nanocrystals are closely packed into superlattice arranged in an almost defect-free 3-D structure. In conclusion, the as-synthesized SAM-SL- UCN nano crystals had tendency to self-assemble into both 2D and 3D owing to their narrow particle-size distribution and uniform particle-sizes.



**Figure 3.4.5: The XRD pattern for three different Exsets (1,2,3) confirming the appearances of major cubic, mixed crystalline and major hexagonal phases, respectively.**

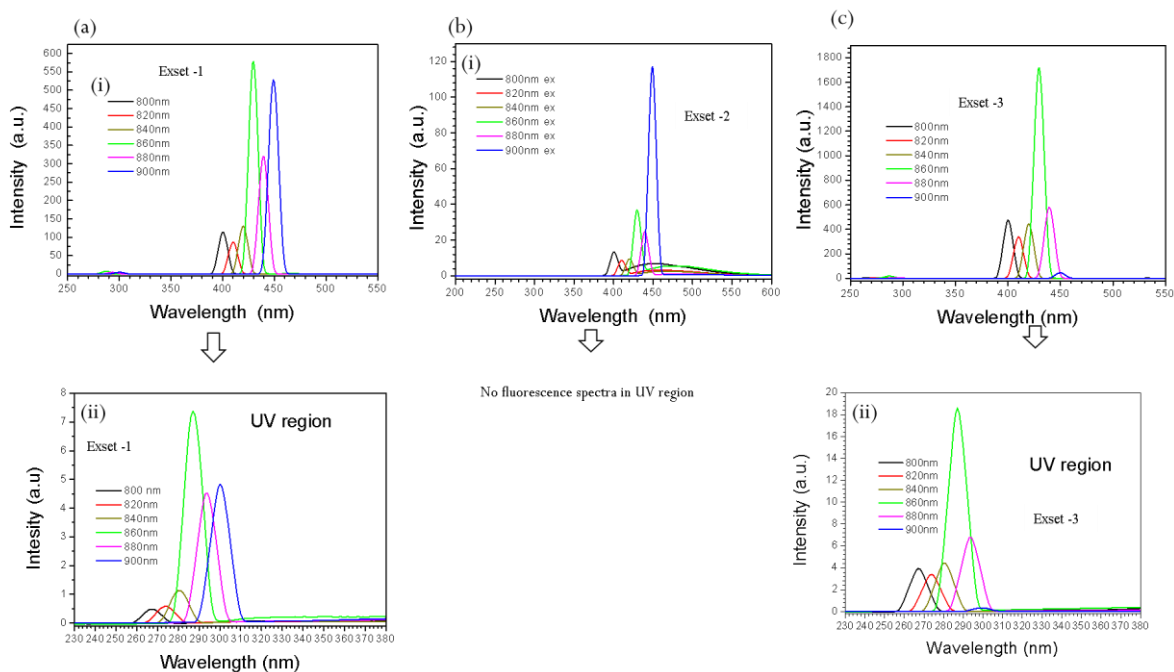
However, TEM analysis for exset-1, exset-2, exset-3 in figure 3.4.1, figure 3.4.2 and figure 3.4.3, respectively, further confirms the formations of complete cubic [(111), (200), (220), (311)] cubic [(111), (200), (220), (311)] and mostly hexagonal phases [(101), (210), (311)], [43]–[47] respectively. The appearances of planes from TEM-SAED pattern for each of the sets are well matched with their resulted diffraction planes received from their corresponding XRD pattern shown in figure 3.4.5. The appearances of those phases have also been confirmed with Raman analysis as discussed in subsequent sections.



**Figure 3.4.6: The Raman analysis strongly indicate the appearances of (a) major cubic (b) cubic and hexagonal (c) major hexagonal phases in exset- 1, 2 and 3 respectively**

The Raman spectra of three different synthesized samples are shown in figure 3.4.6 confirming the presence of phases in synthesized samples. For exset-1 sample (figure 3.4.6a), most of the vibrational modes appear beyond  $700\text{cm}^{-1}$  and confirm the appearance of cubic phases (FCC) conjugated strongly with oleic acid. In sample 2 (figure 3.4.6b), the dominant mode has been appeared near  $275\text{ cm}^{-1}$  confirming the presence of dominant cubic phases. In exset-3 sample, the presence of hexagonal phases have been confirmed with the appearances of vibrational modes with their maximum positions at  $301\text{cm}^{-1}$ ,  $399\text{cm}^{-1}$ ,  $628\text{cm}^{-1}$ ,  $492\text{cm}^{-1}$ ,  $501\text{cm}^{-1}$ ; though presence of cubic phases with Raman spectrum (figure 3.4.6c) has also been traced with  $277\text{cm}^{-1}$  and still we can confirm that most of the cubic phases haven transformed into hexagonal phases in this sample 3. The resulted vibrational modes are closely matched with the previous reported results.[48]–[52] Presence of asymmetry  $\text{CH}_3$ ,  $\text{C-CH}_3/\text{CH}_2$  and O-H stretching modes are assigned by  $1439\text{ cm}^{-1}$ ,  $2854/2896\text{ cm}^{-1}$ ,  $3333\text{cm}^{-1}$  conjugating with oleic acids . Presence of different stretches along with oleic acid has been reported elsewhere[53].

The upconversion fluorescence spectra of three differently synthesized SAM-SL UCNPs are shown in figure 3.4.7a, 3.4.7b and 3.4.7c for exset-1, exset-2, and exset-3, respectively. For exset-1 and exset-3, fluorescence spectra is observed in both of UV and visible wavelength region though intensity of emissions in visible region is much higher than those in UV region. The full range of emission bands are shown in figure 3.4.7a-i and 3.4.7(c-i) and UV ranges are shown in figure 3.4.7a-ii and 3.4.7c-ii for exset-1 and exset-3 samples, respectively. The maximum emission band positions are appeared at 267nm, 274nm, 280nm, 287nm, 294nm, 300nm in UV region and at 400nm, 410nm, 420nm 430nm, 439nm, 449nm in visible region under 800nm, 820nm, 840nm, 860nm, 880nm, 900nm of excitation wavelength in NIR range, respectively, for both synthesized samples (exset-1 and exset-3). And interestingly, clear red shifting has been observed in both of the cases with increasing excitation wavelengths.

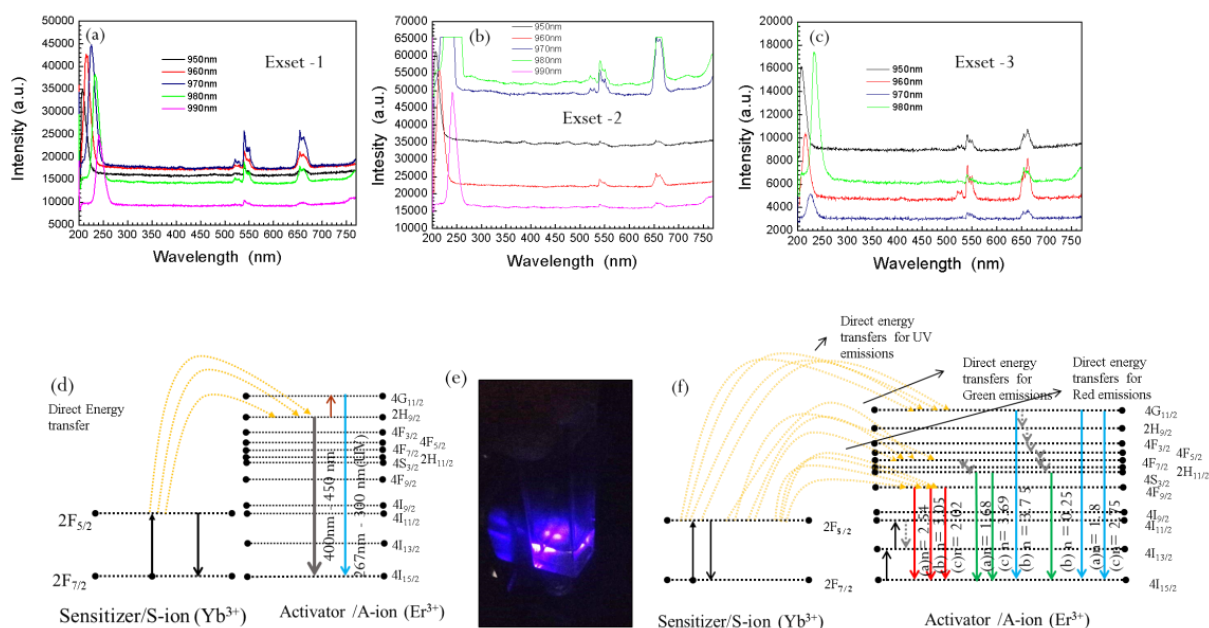


**Figure 3.4.7: Fluorescence spectra recorded at room temperature with changing excitation wavelengths from 800nm to 900nm; Fluorescence with (a) exp. Set up 1 (i) Full region (ii) UV region;(b) exp. Set up 2(only full region is shown, no fluorescence occurred in UV region );(c)exp. Set up 3 (i) Full region (ii) UV region**

Highest intense emissions band are observed under 860nm (for both in UV and visible) NIR excitation wavelength source. However, for the other synthesized sample (with exset-2) emissions are observed only in visible region with appearing highest intense emissions under 900nm NIR excitation wavelength source and hence the maximum emission band positions are appeared at 401nm, 410nm, 421nm, 430nm, 440nm, 449nm with similar trend of shifting with increasing excitation wavelengths. However the fluorescence intensities of the exset-3 sample is much higher and about 2.9 times for UV region and 2.5 times in visible region compared to the exset-1 sample and about 14.7 times in visible region compared to the exset-2 sample with considering the highest intense band positions in each case. In visible region all of the emission spectra lie in between 400nm -450nm satisfying blue emissions and the other emission bands

lay in the UV region. The corresponding energy band diagram is shown in figure 3.4.8d and follows continuous direct energy transfers from  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions. Due to energy transitions  $2F_{7/2}(\text{Yb}^{3+}) - 2F_{5/2}(\text{Yb}^{3+}) - 2H_{9/2}(\text{Er}^{3+}) - 4I_{15/2}(\text{Er}^{3+})$  blue emissions occurred and due to the energy transitions  $2F_{7/2}(\text{Yb}^{3+}) - 2F_{5/2}(\text{Yb}^{3+}) - 2H_{9/2}(\text{Er}^{3+}) - 4G_{11/2}(\text{Er}^{3+}) - 4I_{15/2}(\text{Er}^{3+})$ , the less intense UV emissions occurred. The intense visible blue emission from the as-prepared colloidal SAM-SL-UCNPs solutions in quartz - cuvette is shown in figure 3.4.8e.

**Upconversion luminescence with 140-femtosecond laser pulses (80 MHz repetition rate) under 950-990nm NIR excitation sources:**



**Figure 3.4.8: Fs-laser based upconversion spectra for (a)Exset-1 (b) Exset-2 (c) Exset 3)(d)Energy level diagram of synthesized SAM-SL –UCNPs (e) Intense visible blue emissions under NIR excitation sources (800-900nm). : (f) associated energy level diagram of different SAM-SL-UCNPs under femtosecond laser source**

High energy upconversion luminescence was observed due to the interactions of three SAM-SL-UCNPs colloidal sample-solution with 140-femtosecond laser pulses under different NIR excitation sources. Hence, upconversion emissions in both of the UV and visible region are observed. Emission bands are observed in between 200nm-270nm for UV region and in between 500nm-680nm for visible region in each of three cases.

Remarkable shifting has been occurred in UV region, however in visible region no such shifting have been occurred under different NIR excitation sources. Intense band positions are appeared at 207nm, 215nm, 225nm, 233nm, 241nm for 950nm, 960nm, 970nm, 980nm, 990nm of NIR excitation wavelengths for 2<sup>nd</sup> sample (exset-2). Whether, any distinct bands have not appeared under 970nm and 980nm sources, although for 950nm 960nm, 990nm excitations the distinct bands are appeared. It is further notice that, the corresponding red shifting are occurred by 8nm, 10nm, 8nm and 8nm with increasing excitation wavelengths from 950nm towards 990nm, respectively. The corresponding spectra received under Fs laser treatment is shown in figures 3.4.8 (a-c) for Exsets (1-3), respectively and the schematic of their corresponding energy level diagram is shown in figure 3.4.8f.

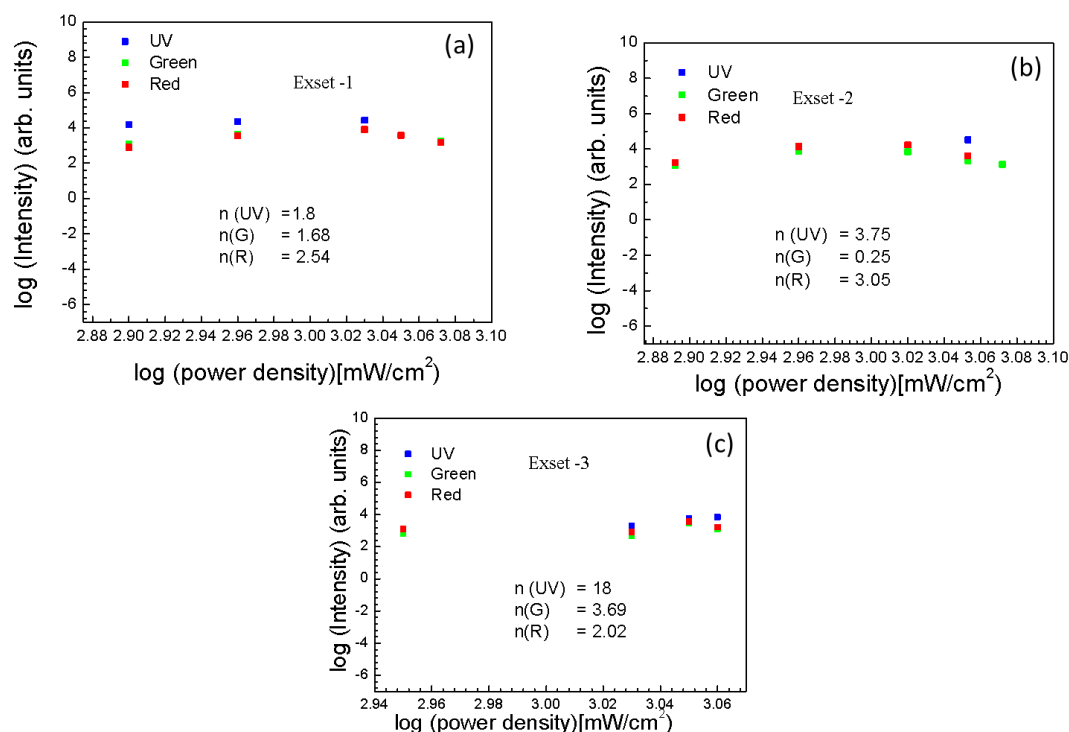
However, no observable band-shifting has been occurred in three different samples rather than emission intensities. Based on the baseline corrections of intensities under different pump wavelengths, the “n” value has been calculated using power law equation (1) [54]–[58],

$$I_{UC} \sim I_{FS}^n \quad (1)$$

Where,  $I_{UC}$  = luminescence intensity

and,  $I_{FS}$  = laser excitation power

‘n’ represents the number of absorbed photons per photon emitted under the Fs-laser excitation power ( $I_{Fs}$ ) and this has been calculated from the slopes of  $\log(I_{UC})$  versus  $\log(I_{Fs})$ (figure 3.4.9) and their values are mentioned in figures 3.4.9a, 3.4.9b, 3.4.9c i.e. for UV, green and red emissions for three different cases. In UV regions, the ‘n’ values have been evaluated to be 1.8, 3.75 and 2.75; in green visible regions, the values are 1.68, 0.25, 3.69; and for red emissions, values are found to be 2.54, 3.05, 2.02 satisfying direct energy transfers from  $Yb^{3+}$  (S-ion) to  $Er^{3+}$  (A-ion) [ $Yb^{3+}$  ( $2F_{5/2}$ ) -  $Er^{3+}$  ( $4G_{11/2}, 4F_{7/2}, 4F_{9/2}$ )].



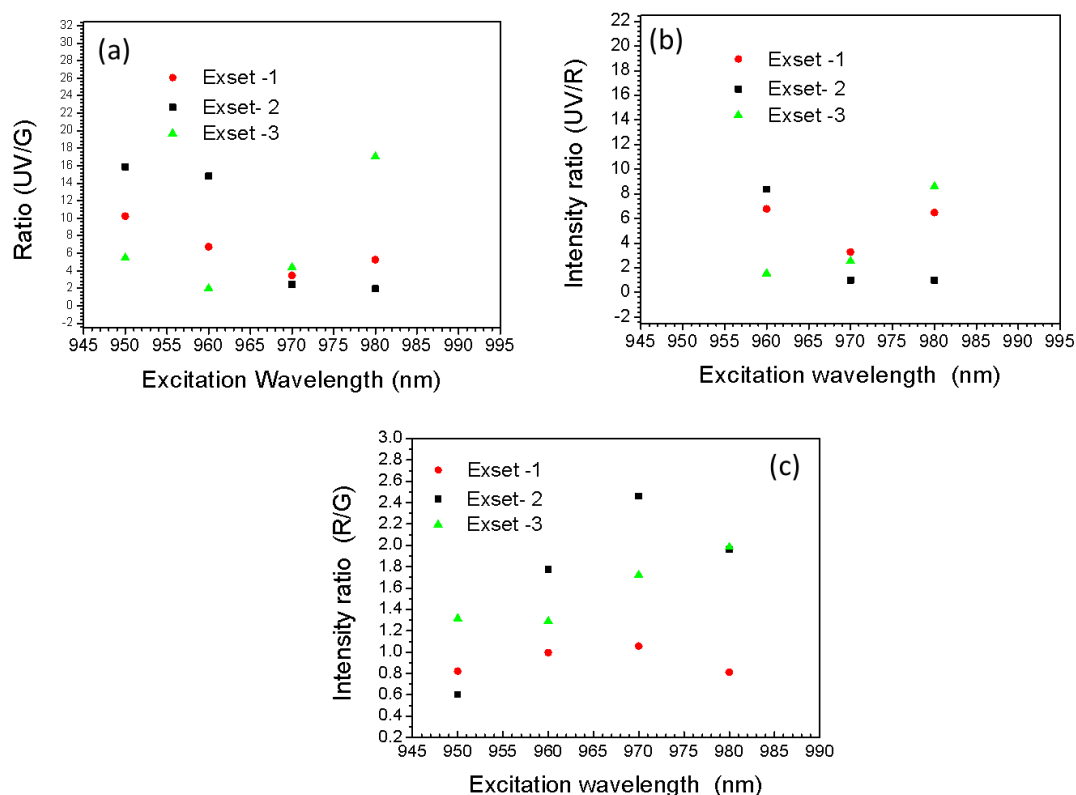
**Figure 3.4.9 : “n” –values received from fs-laser power dependent formula and have been derived in deep UV, green and red visible regions for three Exp. Sets -1, 2 and 3 in (a)(b)(c) , respectively. The highest values occurred for Exset – 3**

It is further found out that most of the “n” values are appeared to be almost = 2 or >2 which further confirmed us that minimum a pair of photons can be transferred from S-ion (sensitizer) to A-ion (activator) for UV, green and red emissions. From figure 3.4.9b, it is confirmed that the ‘n’ value of 0.25 indicates that green emission, for sample 2 (exset-2), does not result for any direct energy transfer, however, it comes due to cross relaxations between energy levels. Based on these results, an energy level

**Table 3.4.1: Tabulated form of “n” values in three different Experimental sets (Exsets) along with their corresponding energy level diagram**

| Parameters                                                | Exset-1<br>(Designated as “a”<br>in figure 3.4.9a)                                                                                                                                                                                 | Exset-2<br>(Designated as “b”<br>in figure 3.4.9b)                                                                                                                                                                                                                                                                                                                        | Exset-3<br>(Designated as “c”<br>in figure 3.4.9c)                                                                                                                                                                                 |
|-----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| “n”- values<br>with their<br>corresponding<br>emissions   | 1.8(UV emission),<br>1.68(G emission),<br>2.54(R emission),                                                                                                                                                                        | 3.75(UV emission),<br>0.25(G emission ),<br>3.05(R emission),                                                                                                                                                                                                                                                                                                             | 18(UV emission),<br>3.69(G emission),<br>2.02(R emission),                                                                                                                                                                         |
| Corresponding<br>energy<br>transfers (UV,<br>Green , Red) | UV emission<br>= $2F_{7/2}-2F_{5/2} - 4G_{11/2}$<br>- $4I_{15/2}$<br><br>G emission= $2F_{7/2}-$<br>$2F_{5/2} - 4F_{7/2}- 2H_{11/2}-$<br>$4S_{3/2}- 4I_{15/2}$<br><br>R emission= $2F_{7/2}-$<br>$2F_{5/2} - 4F_{9/2} - 4I_{15/2}$ | UV emission<br>= $2F_{7/2}-2F_{5/2} - 4G_{11/2}$<br>- $4I_{15/2}$<br><br>G emission(much<br>quenched value) =<br>$2F_{7/2}-2F_{5/2} - 4G_{11/2}$<br>- $2H_{9/2}$<br>- $4F_{3/2}- 4F_{5/2} -$<br>$4F_{7/2}- 2H_{11/2}- 4S_{3/2}-$<br>$4I_{15/2}$ (More no. of<br>non-radiative<br>relaxations present)<br><br>R emission= $2F_{7/2}-$<br>$2F_{5/2} - 4F_{9/2} - 4I_{15/2}$ | UV emission<br>= $2F_{7/2}-2F_{5/2} - 4G_{11/2}$<br>- $4I_{15/2}$<br><br>G emission= $2F_{7/2}-$<br>$2F_{5/2} - 4F_{7/2}- 2H_{11/2}-$<br>$4S_{3/2}- 4I_{15/2}$<br><br>R emission= $2F_{7/2}-$<br>$2F_{5/2} - 4F_{9/2} - 4I_{15/2}$ |

diagram has been drawn to represent the energy transfer and mechanisms which are responsible for the different emissions as it is shown in figure 3.4.8f (The corresponding “n”- values are also associated with the different emissions under three different sets of experiment). Further the energy transition bands, ‘n’ and emission colours have been shown in a tabulated form (table 3.4.1).



**Figure 3.4.10: Ratio plots for the intensities of different emissions of three SAM-SL-UCNPs colloidal solutions with different excitation radiations (a) ratio of UV/Green emission intensity, (b) ratio of UV/Red emission intensity (c) ratio of red/green emission intensity**

**Table 3.4.2: Tabulated form of intensity ratio values in UV and visible region under different excitation wavelengths:**

| UV region                    |           |                                  |                                  | Visible region            |                                       |                 |
|------------------------------|-----------|----------------------------------|----------------------------------|---------------------------|---------------------------------------|-----------------|
| Ex.<br>W.L.<br>( $\lambda$ ) |           | UC<br>intensity<br>( $\lambda$ ) | Ratio<br>values<br>( $\lambda$ ) | Ex. W.L.<br>( $\lambda$ ) | Highest<br>intensity<br>( $\lambda$ ) | Ratio<br>values |
| 960                          | (exset-1) | 25278                            | 2.27                             | 970(G)                    | 7722                                  | 2.79            |
| 970                          |           | 26734                            | 2.40                             | 970(R)                    | 8154                                  | 2.28            |
| 960                          |           | 33235                            | 2.99                             | 980(G)                    | 7112                                  | 2.56            |
| 990                          | (exset-2) | 33422                            | 3.01                             | 970(R)                    | 16923                                 | 4.74            |
| 980                          | (exset-3) | 11098                            | -----                            | 960(G)                    | 2772                                  | -----           |
|                              |           |                                  |                                  | 960(R)                    | 3573                                  |                 |

The efficient populations of photons in different energy levels could be the possible reason of occurring different intense emission bands under NIR sources (950nm-990nm excitation wavelengths). One tabulated form of the intensity ratio values in UV and visible region is shown in table 3.4.2 (with corresponding to figure 3.4.10).

The Quantum yield values (figure 3.4.11) have been determined for different superlattice UCNPs and they are found to be as follows (table 3.4.3, tables 3.4.4, 3.4.5):

**Table 3.4.3: Shows the Quantum Yield (QY) for the different samples**

| Samples | Quantum Yield (QY) |                |
|---------|--------------------|----------------|
|         | UV region          | Vis- region    |
| Exset-1 | 0.032 %-0.22%      | 0.076%-0.22%   |
| Exset-2 | 0.054% - 1.44%     | 0.124% - 1.44% |
| Exset-3 | 0.08% - 1.17%      | 0.19% - 1.17%  |

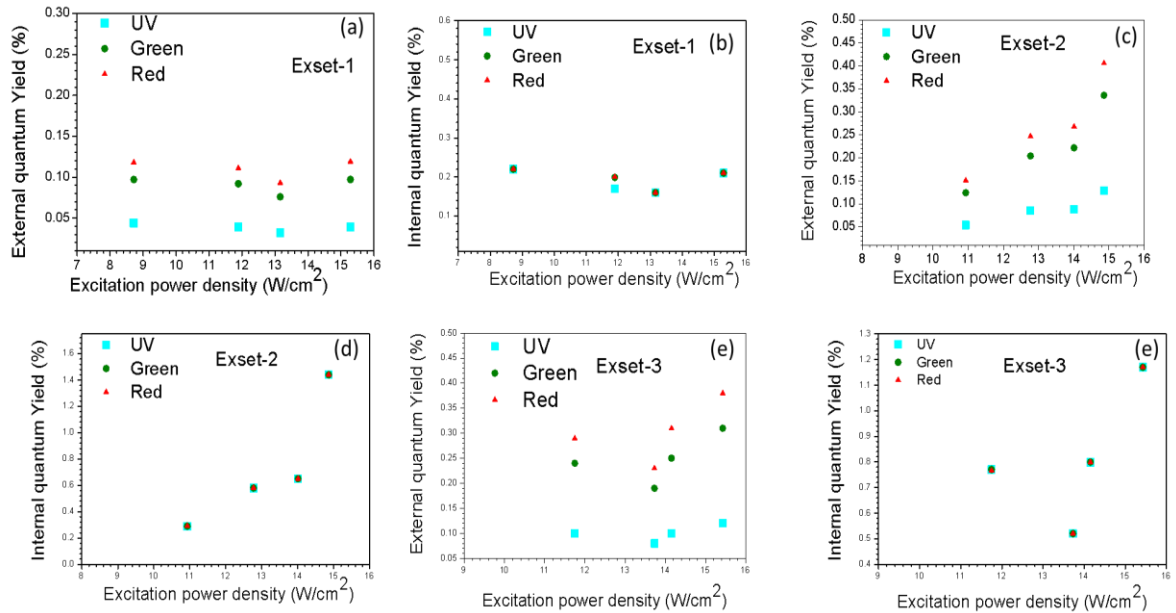
**Tabulated forms of different Quantum yield (Q.Y.) values in three different Experimental sets: (Exsets)**

**Table 3.4.4: Shows the External Quantum yield**

| Q.Y. values          | Exset-1                                                                                                                                              | Exset-2                                                                                                                                              | Exset-3                                                                                                                                            |
|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| External Q.Y. values | UV emission=<br>0.039%( $\lambda_{ex}$ =960nm)<br>0.032%( $\lambda_{ex}$ =970nm)<br>0.039%( $\lambda_{ex}$ =980nm)<br>0.044%( $\lambda_{ex}$ =990nm) | UV emission=<br>0.129%( $\lambda_{ex}$ =950nm)<br>0.088%( $\lambda_{ex}$ =960nm)<br>0.085%( $\lambda_{ex}$ =970nm)<br>0.054%( $\lambda_{ex}$ =980nm) | UV emission=<br>0.12%( $\lambda_{ex}$ =950nm)<br>0.099%( $\lambda_{ex}$ =960nm)<br>0.08%( $\lambda_{ex}$ =970nm)<br>0.103%( $\lambda_{ex}$ =980nm) |
|                      | G emission=<br>0.097%( $\lambda_{ex}$ =960nm)<br>0.076%( $\lambda_{ex}$ =970nm)<br>0.092%( $\lambda_{ex}$ =980nm)<br>0.097%( $\lambda_{ex}$ =990nm)  | G emission=<br>0.336%( $\lambda_{ex}$ =950nm)<br>0.222%( $\lambda_{ex}$ =960nm)<br>0.204%( $\lambda_{ex}$ =970nm)<br>0.124%( $\lambda_{ex}$ =980nm)  | G emission=<br>0.31%( $\lambda_{ex}$ =950nm)<br>0.25%( $\lambda_{ex}$ =960nm)<br>0.19%( $\lambda_{ex}$ =970nm)<br>0.24%( $\lambda_{ex}$ =980nm)    |
|                      | R emission=<br>0.119%( $\lambda_{ex}$ =960nm)<br>0.093%( $\lambda_{ex}$ =970nm)<br>0.111%( $\lambda_{ex}$ =980nm)<br>0.118%( $\lambda_{ex}$ =990nm)  | R emission=<br>0.406%( $\lambda_{ex}$ =950nm)<br>0.268%( $\lambda_{ex}$ =960nm)<br>0.247%( $\lambda_{ex}$ =970nm)<br>0.151%( $\lambda_{ex}$ =980nm)  | R emission=<br>0.38%( $\lambda_{ex}$ =950nm)<br>0.31%( $\lambda_{ex}$ =960nm)<br>0.23%( $\lambda_{ex}$ =970nm)<br>0.29%( $\lambda_{ex}$ =980nm)    |

**Table 3.4.5: Shows the Internal Quantum yield**

| Q.Y. values          | Exset-1                                                                                                                                          | Exset-2                                                                                                                                          | Exset-3                                                                                                                                           |
|----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
| Internal Q.Y. values | UV emission=<br>0.21%( $\lambda_{ex}$ =960nm)<br>0.16%( $\lambda_{ex}$ =970nm)<br>0.17%( $\lambda_{ex}$ =980nm)<br>0.22%( $\lambda_{ex}$ =990nm) | UV emission=<br>1.44%( $\lambda_{ex}$ =950nm)<br>0.65%( $\lambda_{ex}$ =960nm)<br>0.58%( $\lambda_{ex}$ =970nm)<br>0.29%( $\lambda_{ex}$ =980nm) | UV emission=<br>1.17%( $\lambda_{ex}$ =950nm)<br>0.798%( $\lambda_{ex}$ =960nm)<br>0.52%( $\lambda_{ex}$ =970nm)<br>0.77%( $\lambda_{ex}$ =980nm) |
|                      | G emission=<br>0.21%( $\lambda_{ex}$ =960nm)<br>0.16%( $\lambda_{ex}$ =970nm)<br>0.19%( $\lambda_{ex}$ =980nm)<br>0.22%( $\lambda_{ex}$ =990nm)  | G emission=<br>1.44%(950nm)<br>0.65%( $\lambda_{ex}$ =960nm)<br>0.58%( $\lambda_{ex}$ =970nm)<br>0.29%( $\lambda_{ex}$ =980nm)                   | G emission=<br>1.17%( $\lambda_{ex}$ =950nm)<br>0.799%( $\lambda_{ex}$ =960nm)<br>0.52%( $\lambda_{ex}$ =970nm)<br>0.77%( $\lambda_{ex}$ =980nm)  |
|                      | R emission=<br>0.21%( $\lambda_{ex}$ =960nm)<br>0.16%( $\lambda_{ex}$ =970nm)<br>0.20%( $\lambda_{ex}$ =980nm)<br>0.22%( $\lambda_{ex}$ =990nm)  | R emission=<br>1.44%( $\lambda_{ex}$ =950nm)<br>0.65%( $\lambda_{ex}$ =960nm)<br>0.58%( $\lambda_{ex}$ =970nm)<br>0.29%( $\lambda_{ex}$ =980nm)  | R emission=<br>1.17%( $\lambda_{ex}$ =950nm)<br>0.799%( $\lambda_{ex}$ =960nm)<br>0.52%( $\lambda_{ex}$ =970nm)<br>0.766%( $\lambda_{ex}$ =980nm) |



**Figure 3.4.11: Plots for External and internal Quantum yields of Exset-1(a&b), Exset-2(c&d), and Exset-3(e&f), respectively**

### 3.4.3 Discussion:

The synthesized SAM-SL-UCNPs are appeared as an autonomous organization of upconverting nanoparticles without any kind of intervention or using any interfacial assembly method separately as reported earlier.[59] The self-assembled superlattice formations can be considered as static-self-assembly (which are stable after formations). A one-pot chemical synthesis approach was applied for preparation of these UCNPs with narrow particle size distribution (particle size 5-9nm). TEM images have provided direct proof of such formations. The synthesized SAM-SL-UCNPs are stable and did not proclaim any oxidation. The nearly spherical UCNPs had a great tendency to form 2D and 3D superlattice structures. The formations of such 2D and 3D superlattice structure patterns controlling ambient reaction parameters must be having strong importance in several practical applications such as plasmonic metamaterials[60]–[64], solar cells[65], [66], due to their nanoscale-architectures and can also open new windows in bioimaging[67], [68] and photodynamic therapy[69], [70] and so on. The morphologically controlled SAM-SL-UCNPs with bright fluorescence introducing high intense blue emissions and generation of high energy upconversion under femtosecond laser treatment make them unique. The applications of upconversion emissions under different femtosecond irradiations are well known to us[71]–[75]. Now, the combination of self-assembled morphology along with strong upconversion emissions (strong fluorescence under 800nm-900nm NIR irradiations and strong luminescence mainly in UV region under 950nm-990nm NIR irradiations) could open strong applications in bio-fields which is under investigations.

Significant up-conversion properties have been observed in three different structural configurations, exset- 1, exset- 2, exset – 3. In three of the cases, in UV region, emission bands in between 204-265nm have been found with their maximum values appeared at 207nm, 215nm, 225nm, 233nm and 241nm. In visible-region, the emission bands are located ~ 536-560nm (Green emissions) with maximum value at 539nm and

~644-675nm (Red emission) with maximum values at 654nm and 662nm. However, no observable shiftings have been traced with different configurations but obviously these up-conversion properties appeared with different intensity values (calculated with baseline corrections).

In UV region, for exset -1, highest intense upconversion band is observed under 960nm and 970nm excitation wavelength (ex. w.l.). For exset – 2, the maximum intensity observed under 960nm and 990nm ex. w.l. For exset – 3, it was observed under 980 nm excitation.

Considering visible-region, highest upconversion intensities appeared under 970nm, 980nm 960nm ex. w.l. for green emissions in exset -1, exset-2 and exset-3, respectively. Whereas, for red emissions, the maximum intensity values arisen under 970nm, 970nm, 960nm excitation wavelength in exset -1, exset-2 and exset-3 , respectively.

However, for UV section, in exset-1, the highest upconversion intensity has been appeared to be 2.27 (960nm excitation), 2.4(970nm excitation) times higher compared to that in exset-3(980nm excitation); while in exset-2, the highest upconversion intensity appeared to be 2.99 (960nm excitation), 3.01(990nm excitation) times higher compared to that in exset-3(980nm excitation).

In visible-emission wavelength section, for exset-1 and exset-2, highest up-conversion intensity has been emerged to be 2.79 (970nm excitation), 2.56 (980nm excitation) times higher, respectively, for green emissions and 2.28(970nm excitation), 4.74(970nm excitation) times higher, respectively, for red emission compared to those in exset-3(960nm excitation)

Delayed nucleation path has been maintained for synthesising cubic ( $\alpha$ ) and hexagonal ( $\beta$ ) phase UCNPs from their corresponding rare-earth precursors. Hence, growth process of both phases ( $\alpha$  and  $\beta$ ) and transition operation ( $\alpha$ - $\beta$ ) have been disclosed with XRD, TEM, Fluorescence/Luminescence techniques. Several analyses direct us, UC emission was influenced by the growth of superlattice nanocrystals, and more specifically, emission intensity was affected owing to nucleation and phase-transition operations. Moreover, different emissive intensity ratios found to be sensitive with different phases-appearances in three formations of exset-1,2,3.

However, a prolonged heat treatment method could be the reason of appearing different uniform, monodisperse SAMUCNPs which followed four steps (figure 3.4.12) during synthesis, they are (i) A delayed - nucleation (ii) Growth with imparting monomers (iii) size-depletion and, (iv) Accumulation. Hence, as the heat treatment was continued to 20 mins, cubic ( $\alpha$ ) UCN-phases started to arise in solution and further with a prolonged time a turbid solution was formed confining a modest increment of nanocrystal-sizes. The co-precipitation between rare-earth precursors and NaF developed  $\alpha$ -phased nanocrystals. A sufficient amount of decomposed NaF could fast the growth rate of monomers ( $\alpha$ -NaYF<sub>4</sub>: Yb, Er) whose concentration became high after a certain time-interval. During this period, the monomers maintained their uniformity in solution (say, in exset-1) by manifesting (111), (100) planes as admitted with HRTEM images. These facets were sustained by strong binding of major capping agents on crystal-surface ( $\text{RE}^{3+}$  and  $\text{COO}^-$ ). Afterwards, the exhausting and stabilizing nature of monomers was revealed while the monomer-size remained invariant. This condition, could occur while they consumed entirely in solution with restricting Ostwald's-ripening process[76]–[78]. This situation could be happened due to appearance of weak van der Waal's forces of interactions between capping agent (oleic acid) molecules and  $\text{RE}^{3+}$  ions on nanocrystal-surfaces.

Further,  $\alpha$ - $\beta$  phase transition started to arrive in solution (say, in exset-2) with a further prolonged heat treatment by allowing dissolution and recrystallization followed by Ostwald-ripening process. Hence, a complete  $\alpha - \beta$  phase transition took place (say, in exset -3).

Additionally, in present investigation, it can be seen that the highest upconversion intensity ( $I_{HUC}$ ) has been affected by the appearances of  $\alpha/\beta$ /mixed crystalline phases and appeared to be maximum in both UV and visible region while accumulated mixed phases ( $\alpha$  and  $\beta$ ) in solution. The red to green emission ratios ( $f_{r/g}$ ) has been found to be 1.06, 2.38, 1.28 for cubic, mixed and hexagonal phases, respectively i.e. highest in mixed occurrence (say, exset-2). Moreover, the,  $\alpha - \beta$  phase transition operation can be considered to be a delayed nucleation growth process with accumulating sufficient amount of  $\alpha$ -UCN monomers.

The two factors- surface - reaction and diffusion of monomers, which has influenced the growth of nanocrystals. Hence, the growth of nanocrystals could be expressed as [79], [80];

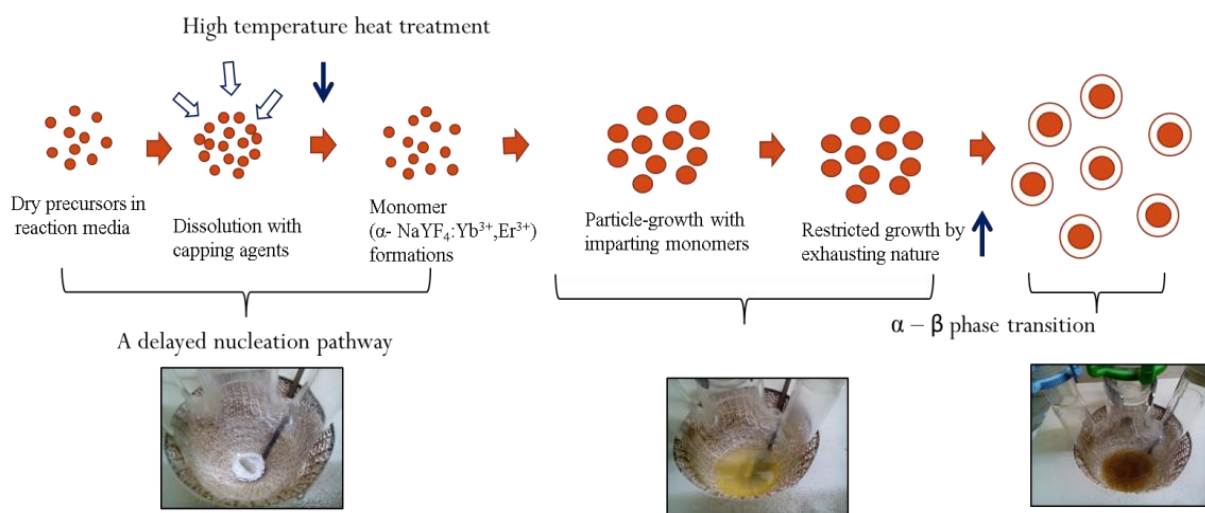
$$J = 4\pi b^2 \gamma \frac{dC}{db} \quad (2)$$

Where,  $b$ = radius of plane through which the flux ( $J$ ) can pass

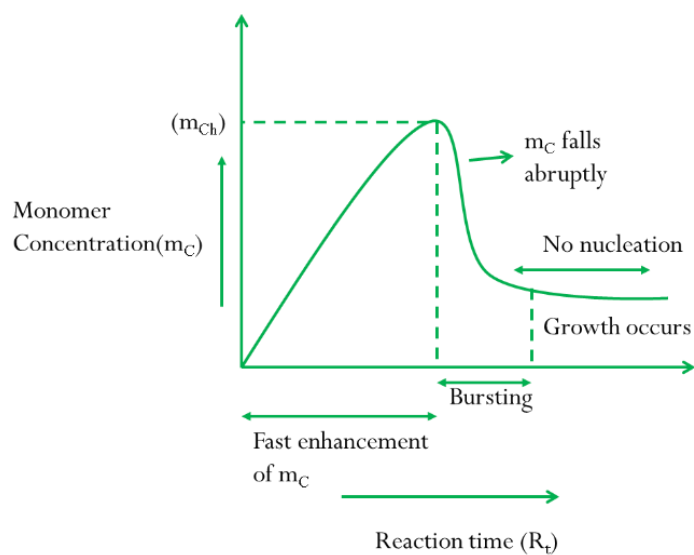
$\gamma$  = Diffusional co eff.

$C$ = Monomers concentration at a length  $b$ '

Concerning several literature on nucleation and growth of nanocrystals, it can be concluded that it could be possible to occur nucleation and growth of nanocrystals simultaneously as described by Finke-Watzky mechanism [81–84] where a nucleation ( $P - Q$ ) would happen leisurely and an autocatalytic crystal-growth ( $P+Q= 2Q$ ) would



**Figure 3.4.12: A schematic of the whole process succeeding the nucleation and growth mechanism along with  $\alpha - \beta$  phase transition. The corresponding exp. investigations are also placed.**



**Figure 3.4.13: The mechanism associated with the formation of monomers and particle-growth**

take place. The principal theory of leisure nucleation and autocatalytic growth process would follow Lamer Mechanism [85], [86] (figure 3.4.13) which completes in three steps to separate nucleation and growth into distinct stages. The following stages are: (1) A fast enhancement of monomer – concentration, (2) Burst in nucleation after a certain period of reaction-minimizing monomer-concentration abruptly and (3) afterwards, growth arises by diffusing nucleates in solution.

Furthermore, UCN superlattices with different architecture and periodicity are the high ordered UCN superlattice exhibited leads to the variation of quantum yields. However,  $I_{UC}$  and  $f_{r/g}$  is influenced by the amount  $\alpha$  and  $\beta$  contents in synthesized nanocrystals. It can also be believed that the phase-controlled SAMUCNPs bearing high quality crystal which could be potential candidates for making sensors, emitters and display techniques along with several bio imaging and bio-medicines.

#### **3.4.4 Summary and Conclusions of PART IV:**

In this work, we report that under different reaction conditions, NaYF<sub>4</sub> based UCNP were able to develop several self-assembled super lattice structures (as confirmed by different TEM images) with exhibiting bright fluorescence under CW 980 nm NIR and luminescence under 140 femtosecond laser treatment. By applying different synthetic conditions, the fluorescence and luminescence properties are well tuned with differently synthesized self-assembled structures. The SAMSLs are confined with a few soft ligands or capping agents and it is believed that presence or alignment of them along with the bulk material play an important role in tuning their optical properties. In summary, we have synthesized three different UCN-SL structures and examined all properties on their colloidal solutions. The increment of high reaction temperature induced more amount of hexagonal phases compared to its cubic. Hence, the number of absorbed photon per emission has been calculated for each of the emission [e.g. UV, Visible (Green, Red)] individually and has been found to be 1.5 - 5.

The intensity ratios have been plotted as UV/Green, UV/Red, Red /Green for three sets of experimental samples. Further, the quantum yield values (for both internal and external Q.Y. values) have also been enumerated along with several excitation power densities vs Q.Y. plots for each of the emissions received under Fs –laser facility and these values lie in the range between 0.032 %(Min) - 1.44 % (Max). The growth mechanism of the UCN-SLs structures (from Exset-1 - Exset-3) has also been scrutinized along with phase-transition (monomers - monodispersed NPs) (The schematic in figure 3.4.12 shows the entire growth) process. So, moreover, by observing optical properties and Q.Y. values we can assure that the shape directed assembling strategy of the synthesized nanocrystals can promote the bio and energy related nanophosphor applications.

## **4 SUMMARY, CONCLUSIONS AND SCOPE of this WORK**

In this chapter, the **summary and conclusions** of the present dissertation have been elucidated. The whole dissertation consists of four chapters-Introduction, Experimental section, Results and Discussion, and summary and conclusions section. The third chapter (results and discussion part) is sub-divided into five parts. A short summary is given on those four chapters:

**Chapter 1:** This chapter presents the background of UCNPs (synthesis, characterizations and their applications) with introducing literature reviews. At the end of this chapter the motivation and objectives of the present dissertation have been explained.

**Chapter 2:** This chapter deals with the experimental part, which includes basis principles of different characterization techniques, synthesis methods, and materials used to complete the present dissertation work. The synthesis methods to prepare different morphological UCNPs have been described in detail. To synthesize  $\alpha$  and  $\beta$  -NaYF<sub>4</sub> upconverting nanocrystals three different hexahydrate precursors have been used in hot-surfactant solutions and details of those precursors have also been mentioned in this section. UCN-hexagonal, UCN-dots, UCN-Ds, SAM-SL-UCNPs have been synthesized in unique pathways following thermal decompositions solvothermal treatments. In each of the cases, the reaction parameters were varied in a precisely controlled way to form monodisperse and self-assembled nanocrystals which were identified and confirmed with different characterization techniques. During synthesis, the successive growth stages of nanocrystals are- Nucleation, Particle growth, Dissolution resulting contracting particle sizes, and Aggregation. The  $\alpha$  to  $\beta$ -phase transition i.e. transition from  $\alpha$ -UCNPs (NaYF<sub>4</sub>: Yb, Er - monomers) to  $\beta$ -UCNPs (NaYF<sub>4</sub>: Yb, Er – monodisperse nanoparticles occurs by amplifying or limiting Ostwald-ripening process. Precursor-decomposition took place around 100°C of mantle- reaction temperature and under this condition, the carbon species (fluorinated / oxyfluorinated) started to release from solution. Beyond 20 mins of reaction time, the  $\alpha$ -phases started to appear in solution. However, a delayed nucleation pathway is required to synthesize monodisperse UCNPs rather than a rapid nucleation pathway. For nucleation, the reaction temperature controls the crystallite size. The co-precipitation between decomposed NaF and rare earth precursors results in formations of  $\alpha$ -NaYF<sub>4</sub> as accumulation of NaF in solution can burst nucleation and can fast the growth rate of  $\alpha$ -NaYF<sub>4</sub> nanocrystals, immediately nanocrystal-sizes enhance. However, decomposition rate of NaF in solution increases with increasing temperature but is

independent of precursor's concentration. During this period, the monomer concentration ( $\alpha$ -NaYF<sub>4</sub>- concentration) becomes high by obstructing Ostwald ripening process and exposing (111) and (100) facets in nanocrystals and afterwards, nanocrystal-size remains invariant which further reveals the unstable and exhausting behavior of monomers owing to reduced bonding-integration (probably dominant van der Waal's interactions between oleic acid and nanocrystal surface). While all the monomers consume entirely (nanoparticle size distribution becomes broadened during this period), with time being, dissolution and recrystallization start to occur in solution with stimulating Ostwald ripening process owing to broadened size distribution. In this dissolution and recrystallization process, the  $\alpha$  to  $\beta$  phase transition starts to appear.

More importantly, the presence of  $\alpha$  and  $\beta$ -phases in differently synthesized UCNPs affected different upconversion emission spectra (fluorescence, luminescence, photoluminescence) resulting in different intensity-ratio values.

**In 3<sup>rd</sup> chapter, part I**, high quality hexagonal UCNPs have been synthesized with uniform size distribution. Emission properties were tuned controlling reaction parameters and have been found to be highly efficient. The synthesized NaYF<sub>4</sub> nanocrystals with Yb<sup>3+</sup> and Er<sup>3+</sup> have been proven to be the best UCNPs reported ever in literature because they are able to show emission even after decreasing the laser power density below 50 mW/cm<sup>2</sup>.

**In 3<sup>rd</sup> chapter, part II**, UCN-dots have been synthesized with thermal decomposition of lanthanide precursors. The average particle size has been found to be 3.4 nm in diameter which are smallest in size reported ever and are stable for a minimum of one year exhibiting upconversion emissions. This work further revealed the emission of UV luminescence from synthesized UCN-dots under interaction with femtosecond laser of 140 femtosecond pulsed at 80 MHz repetition rate.

**In 3<sup>rd</sup> chapter, part III**, controlling reaction parameters in in-situ condition and without incorporating any external dendritic polymers during synthesis, Upconverting nanodendrites (UCN-Ds) have been developed for the first time. UCN-Ds contain both of the  $\alpha$ - and  $\beta$ -phase within its solid structure and are very stable (up to a minimum of 2 years). Presence of these two phases in dendritic UCNP could be the cause of high energy upconversion and make them very seminal and are with caterpillar/necklace type of structure.

**In 3<sup>rd</sup> chapter, part IV**, the formations of self-assembled-superlattices of upconverting nanophosphors over multiple-magnified scales prepared by one-pot chemical approach is reported. The different types nanoparticle superlattice have been constituted through the bottom-up self-assembly approach where the process is either in an equilibrium or in a non-equilibrium state. The synthesis method is optimized with a minimum amount of heating rate.

The upconversion emissions at ultraviolet and visible emissions have been investigated. The synthesis procedure applied here to form UCN-SL is a modified approach of the synthesis method developed by our group previously. The entire reaction process was carried out in an inert gas (Argon) atmosphere. The different self-assembly superlattice structures have been formed in-situ with varying the conditions. The as-synthesized nanophosphors can display sharp and bright luminescence (both in ultraviolet and visible region) and fluorescence (mostly in visible region) under Ti-Sapphire 140-femtosecond laser pulses at 80 MHz repetition rate with 950nm-990nm excitation wavelengths and under 980nm continuous wave laser sources, respectively.

The beauty of our process is that the entire synthesis process consumes less time to obtain the self-assembled UCN-SL structures. Further, how the UCN-SL with different architecture exhibited different upconversion luminescence properties also have been

elucidated. As-synthesized UCN-SL structures represented here are not only to generate new physical properties from bulk materials but also new phenomenon for interactions between particles at nanoscale have also been found out. In order to produce the particular self-assembled UCN-SL pattern in synthesized nano- material we followed few controlled reaction parameters. By applying those key factors, the correlative arrangements of nanocrystal building blocks with their sizes and the spacing between those crystals are maintained in a self-assembled long-range order. The precisely engineered nanocrystal sizes and systematic shaped-assembly treat as building blocks to generate improved entities. Additionally, for the different UCN-SLs the different in intensity of emission and their position and shifting, internal upconversion quantum yield (Internal UCQY) and external upconversion quantum yield (External UCQY), photoluminescence behaviour, fs-laser power dependent luminescence and the number of absorbed photons taking part in the process ( $n$ , where 'n' is the number of absorbed NIR photons per emission under fs-laser excitation power) have been calculated. The controlled morphology with efficient upconversion fluorescence and luminescence of these UCN-SL structures may discover considerable applications in different fields such as lasers, diodes, display-techniques and energy – related applications. The mean particle-sizes are varied from 5nm-8nm. The substantially improved design of nanophosphors will boost biological and energy related nanophosphor applications.

In differently synthesized UCNPs, size and phases have been controlled to achieve multicolor tuned emissions. In previous study on UCNPs and their applications, different methods have been applied to enhance upconversion efficiency by optimizing precursors concentrations and local chemical environment and modifying morphologies. It has always been spellbinding to improve anti-Stokes luminescence in rare-earth dopes nanoparticles owing to their several applications in display devices, lasers, bio-imaging, labeling and sensing and sustaining with eminent photo stability, NIR-to-visible upconversion and long luminescence-lifetime which can make them potential candidates for competitive bio-labels even in commercial purposes.

The energy transferred from sensitizer ( $\text{Yb}^{3+}$  for  $\text{NaYF}_4:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  nanocrystals) to activator ion ( $\text{Er}^{3+}$  for  $\text{NaYF}_4:\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$  nanocrystals) can also be tuned with respect to upconversion enhancement (in each of the synthesized UCNPs different energy level diagrams to represent the transferred energy from sensitizer to activator ions are introduced).

### **Scope for future work on synthesized materials:**

In part I, the synthesized UCNPs have huge responses for applications in display technologies and lasers. In part V, the formations of thin-films could be useful further for making laser devices and smart cards for detection purposes.

In part II, III, and IV the synthesized UCN-nano-dots below 5 nm, self-assembled dendritic (chain/necklace types) and UCN-SL have never been reported respectively. Up-conversion at UV region has never been reported. These combinations in material make them unique under different circumstances and none of the work reported on the femtosecond laser study and properties. Thus these works carry a huge novelty. Previously, our research group reported a couple of works on upconverting materials including UCN-core shell materials with therapeutic applications. Therefore, we strongly believe that UCN-dots and UCN-Ds and SAM-UCN-SL materials reported here with unique sizes and morphologies could be potential candidate for optoelectronic devices and for therapeutic applications. It can be further noted that smaller sizes of nano particles are acceptable much more by the living cells and if size is below 8 nm, then they can be easily excreted through kidney which actually much more important for the use of nanomaterials/this type of materials for therapeutic applications. So, in such case synthesized UCN-dots could be a perfect candidate.

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*by* Monami Das Modak

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